Geochemical Analysis of Waters in a Tropical Glacial Valley, Cordillera Blanca, Peru

A Senior Honors Thesis

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Abstract

The Cordillera Blanca, located in the central Andes of Peru, is the most glacierized mountain range in the tropics. Most of the Peruvian population lives in the arid Pacific plains which are heavily dependent on glacial melt and runoff from these mountains, especially during the dry season. Thus understanding the current physical and chemical hydrology of the region is imperative for making future predictions about climate impacts. The objective of this study is to examine a variety of geochemical parameters in a glacial valley and to determine how and why these parameters vary with elevation and between groups (surface water vs. groundwater). During the dry season of July 2009, surface water and groundwater samples were collected from the proglacial zone of Quilcayhuanca valley, a basin that is 20% glacierized and drains an area of 90 km^2. The water samples from the valley (n=25) were analyzed for major cations (Ca, Mg, Na, K, Fe(II)), major anions (F, Cl, SO_4), nutrients (total N, total P, and Si), and stable isotopes of water ($\delta^{18}O$, $\delta^{2}H$). Field measurements like pH, conductivity, and temperature were also collected. The valley's acidic waters (pH 3-4) are dominated by the major ions Ca^{2+}, Mg^{2+}, and SO_4^{2-}, the last of which is a remnant of pyrite oxidation. Total P and total N show no trend with elevation while Si generally increases with decreasing elevation. Groundwater samples are differentiated from surface water samples by lower pH, specific conductance, and total P and higher Na^{+}, K^{+}, HCO_3^{-}, Si, and $\delta^{18}O$. Using a simple, two end-member mixing model the surface waters leaving the valley at the last site in the drainage basin were calculated to be a mixture of approximately two-thirds surface water (mostly glacial melt) and one-third groundwater.

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Introduction

Mountain glaciers play an important role in water resources for many regions and people. Worldwide glaciers contribute ~0.6 – 1.0% to the global annual runoff, which is thought to be ~4.6 x 10^{13} m^3/yr (Holland, 1978). It is estimated that over 80% of the water supply for arid to semi-arid regions of the subtropics originates in mountainous regions, affecting more than 50% of the world's population (Messerli, 2001). Rapid glacial retreat in the tropical Andes due to a changing climate will have significant consequences for mountain glaciers and the people who rely on glacially-fed water supplies (Bradley, 2006; Vuille *et al*., 2008). Among other effects, climate change and glacial recession threaten to decrease dry season discharge in these regions (Barnett *et al*., 2005).

In the seasonally arid climate of the tropical Andes, glacier meltwater buffers discharge throughout the year and provides greater overall discharge (Mark *et al.*, 2007). So during dry seasons or droughts, glacial meltwater is especially crucial for water resources. Droughts during dry seasons have been predicted for regions that rely heavily on glacial meltwater as a primary water resource (IPCC, 2007).

The Cordillera Blanca, located in the central Andes of Peru, contains about 70% of the world's tropical glacier area (Vuille *et al*., 2008). Most of the Peruvian population lives along the Pacific coastal plains and western slopes of the Andes where the land is arid and heavily reliant on water runoff from the mountains (Vergara *et al*., 2007). Thus, understanding the current physical and chemical hydrology of the region is imperative for making future predictions about climate impacts. Quantifying the role of glacier meltwater and groundwater in terms of the quantity and quality of water available to people is of particular concern.

The impact of melting glaciers on the hydrological cycle has been quantified on a regional scale, but more detailed, valley-specific analyses are required to characterize the geological controls and variability of water quality and stream discharge accurately (Mark *et al*., 2005). An understanding of these geological and hydrological controls is beneficial for the utilization of mixing models which can be used to determine relative contributions from end-members like precipitation, groundwater, and glacial melt. This case study focuses on the hydrochemistry of waters in the glacial valley Quilcayhuanca during the dry season, when precipitation is minimal and the relative glacier melt contribution to streams has been shown to predominate (Mark *et al*., 2003). Although glacial melt has been shown to be important, groundwater is still a predominant component in the Cordillera Blanca (Baraer *et al*., 2009) even though many existing models oversimplify the role of groundwater in glacial environments (Hood *et al*., 2006).

A glacial environment is usually subdivided into different zones including the supraglacial (above), englacial (within), subglacial (underneath), and proglacial zones. The proglacial zone is a mosaic of moraines and other deposits related to glacial advance, retreat, and hydrology (Tranter, 2005). The proglacial zone has the potential for high geochemical activity, because it contains a variety of comminuted glacial debris, is subject to reworking by glaciofluvial activity, and can be colonized by vegetation. Waters traveling through sediment in this area mainly acquire new solutes via sulfide oxidation and carbonate dissolution (Anderson *et al*., 2000; Cooper *et al*., 2002). Furthermore, the concentration of solutes in the proglacial zone is normally higher than solute concentrations of glacial runoff (Tranter, 2005). Natural springs and low-gradient, low permeability plains called pampas are the main sources of groundwater in the proglacial zone of Quilcayhuanca valley. The hydrochemical properties of springs and

pampas are still somewhat mysterious in glacial environments and warrant further study, especially in comparison with surface waters thought to be mainly derived from glacial melt.

This case study seeks to examine a variety of geochemical parameters and determine how and why these parameters vary with elevation and between groups (surface water vs. groundwater). The first objective of this study is to understand the geology and hydrology of Quilcayhuanca valley and relate this knowledge to the hydrochemistry of surface water samples in the proglacial zone. The next objective is to examine how these hydrochemical parameters vary within the valley as waters move from high elevation lakes, through moraines and glacial deposits, and ultimately to the city of Huaraz. Variation between groups of samples (principal channel surface water, tributaries, and groundwater) can be examined for patterns which can be used in hydrochemical mixing models. A hydrochemical distinction between groundwater and surface water is possible with the parameters used in this study. The third and final objective is to use simple, two end-member mixing models to determine relative fractions of surface water and groundwater for the principal channel leaving the Quilcayhuanca drainage basin.

Study Area

Quilcayhuanca valley is part of the Cordillera Blanca, the most glacierized tropical mountain range on Earth, which spans over 120 km between 8.5°-10° S latitude in Peru. The range strikes northwest – southeast and separates stream runoff between the Pacific and Atlantic oceans (Mark and Seltzer, 2003). Figure 1a is a map of the Cordillera Blanca, slightly modified from Mark and McKenzie (2007), which shows the location of Quilcayhuanca. Between 1970 and 2003 the surface area of glaciers in the Cordillera Blanca has decreased from 723 km^2 to 597

km^2, a 22% loss (Racovitneau *et al.,* 2008). Future climate scenarios predict that these glaciers could disappear completely by 2200 (Pouyaud, 2004).

Waters originating from the Quilcayhuanca basin drain into the Rio Santa just outside of the city of Huaraz (population ~ 140,000). The Rio Santa drains the Cajellon de Huaylas watershed (4900 km^2) which captures runoff from the western side of the Cordillera Blanca and eastern side of the nonglacierized Cordillera Negra. Originating at Laguna Conococha, the Rio Santa travels over 300 km to the Pacific Coast, descending from 4300 m and draining a watershed of 12,200 km^2. In Peru the Rio Santa has the second largest discharge of rivers draining to the Pacific coast and also the most regular monthly flow (Mark and Seltzer, 2003). Discharge measurements at various points in the Rio Santa show a marked seasonal discharge pattern (Baraer *et al*., 2009).

Quilcayhuanca valley has a drainage area of 90 km^2 and has no gauged streams. Based on satellite imagery from 2009, the basin is approximately 20% glacierized. The valley has a distinct "Y" shape. In later discussions and Tables the right-lateral branch of the upper valley will be referred to as Quil-R while the left-lateral branch will be referred to as Quil-L. The main section of the valley where the two upper branches merge will be referred to as Quil-M. Samples were divided into three hydrologic groups to look at patterns with elevation: (1) Quil Streams, represented in figures by blue-filled circles, is the group of sampling sites (n=14) from principal stream channels in each of the three valley sections; (2) the Tributaries group, represented by green-filled squares, is composed of tributary samples (n=8) in each of the three sections of the valley; and (3) the groundwater group, represented by red-filled triangles, is composed of groundwater samples (n=3) taken from springs. Figure 2a is a geologic map of the Quilcayhuanca watershed. Figure 2b is a hillshade of a Light Detection and Ranging (LiDAR)

digital elevation model (DEM), zoomed in on the upper portion of the valley. The purple line on Figure 2b represents the contact between two different geologic formations. In both Figure 2a and 2b sampling locations are plotted with symbols appropriate to their grouping and their site number.

The valley geology is dominated by metasedimentary and intrusive igneous rocks. The Jurassic Chicama formation (14% of basin area) dominates the upper portion of the valley. It contains metamorphic sedimentary rocks of Jurassic age characterized by weathered shale, argillite, sandstone, and pyrite. Intrusive rocks (43% of basin area) dominate the high, steep walls of the mid to lower-valley. This intrusive body is mostly characterized as granodiorite and tonalite. Quaternary moraines, glaciolacustrine deposits, glaciofluvial deposits, and pampas compose the remainder of the valley (15% of basin area). Pampas are defined as low-gradient areas that formed from paludified moraine dammed lakes. The pampas are composed mostly of low-permeability, organic-rich, unconsolidated material (Mark and McKenzie, 2007). In terms of hydrochemistry, glacial deposits, fluvial deposits, and pampas are important geological components since they sit on the valley floor, having extensive contact with groundwater and surface water.

Two large proglacial glacial lakes, Cuchillacocha (0.14 km^2) and Tuplacocha (0.46 km^2), sit just in front of glaciers in Quil-R. There are no major lakes in Quil-L. Tributaries were sampled in both upper sections. In Quil-R samples were taken from two tributaries (sites #2 and #3) thought to be draining a high elevation groundwater storage area called Jatun. In Quil-L samples were taken from tributaries on either side of the valley. In general, waters in the upper portion of the valley flow over bedrock, through moraines, and though fluvial deposits. Once the waters enter Quil-M they are mostly flowing through pampas. Waters draining from

Quilcayhuanca valley begin to flow down a steeper path to the city of Huaraz. However, before the waters from Quilcayhuanca reach Huaraz, they merge with streams from two adjacent valleys. The most downstream water sample, site Quilcay (#25), was taken at a point just above the city of Huaraz, approximately 2 km before the stream enters the Rio Santa.

Methodology

Sample Collection and Analysis

Water samples (n=25) were collected in Quilcayhuanca valley during a three day period of the dry season (July 15-17, 2009). Samples for major ions (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, Fe^{2+}+Fe^{3+}, F^{-}, Cl^{-}, and SO_4^{2-}), nutrients (total Phosphorus (P), total Nitrogen (N), and Silica (Si)), and stable isotopes ($\delta^{18}O$, $\delta^{2}H$) were filtered into new HDPE 60 mL Nalgene bottles using a 60 mL HDPE syringe and a 0.45 μm pore-size Nucleopore screw-on filter. Samples were filtered in order to remove suspended sediment. Water samples were subsequently stored in a dark, cool place until analysis. The locations of the samples were recorded using a handheld GPS unit. Additional water quality data were collected using a YSI Multimeter Probe. This instrument measured temperature, pH, and specific conductance. A few sites do not include all of these measurements due to time constraints and availability of the device. Between July 14-15, the site Quil Bel Conf was sampled every hour for 24 hours to observe the diurnal variations. Additional water samples (n=11), but not field measurements, were taken along the Rio Santa and Cordillera Negra (n=4) for comparison with Quilcayhuanca samples.

Concentrations of major ions were measured at McGill University using ion chromatography. Ion concentrations were initially reported in parts per million (ppm) and then converted to milligrams per liter (mg/L) because these two units of concentration are

interchangeable for dilute solutions when the total concentration of ions is less than 7,000 mg/L (Bair and Lahm, 2006). The concentrations were then converted to milliequivalents per liter (meq/L) to examine charge balance. All freshwater samples should be electrically neutral with respect to concentrations of anions and cations, so the sum of the cations (TZ+) in meq/L should equal the sum of the anions (TZ-) in meq/L. The percent difference between the TZ+ and TZ- describes the degree to which this balance is achieved and is described by the equation:

$$PercentDifference = \frac{(TZ+) - (TZ-)}{(TZ+) + (TZ-)} \times 100$$

A positive result indicates that excess cations or insufficient anions exist in the water analysis. A negative result indicates that excess anions or insufficient cations exist in the water analysis (Bair and Lahm, 2006). Bicarbonate (HCO_3^-) was calculated as the difference in the solution charge balance. In other words, if the percent difference from the equation above was greater than 0%, then this percentage was attributed to the bicarbonate ion. The concentration of hydrogen ions [H+] was also included using the relationship $pH = -\log_{10}[H+]$.

Concentrations of nutrients (total P, total N, and Si) were measured using the Skalar San^{++} Automated Wet Chemistry Analyzer in the School of Earth Sciences at The Ohio State University. Total P is a combination of three forms of phosphorus: orthophosphates, polyphosphates, and organic phosphorus. Values were reported as parts per billion (ppb) P as PO_4^{3-}. Duplicate samples analyzed for total P had an average precision of 3%. Total N includes organic nitrogen, ammonia, and nitrate plus nitrite. Total N was reported as ppb N as NO_3^-. Duplicate samples analyzed for total N had an average precision of 11%. Silica values were reported as ppb Si as SiO_2. Duplicate samples analyzed for Si had an average precision of 1%.

Stable isotopes of water were measured at Byrd Polar Research Center at The Ohio State University using mass spectroscopy (Finnigan MAT Delta Plus coupled to a HDO water

equilibrator). Stable isotopes are reported using the δ-notation reported relative to the Vienna-Standard Mean Ocean Water (VSMOW) standard, with accuracy of ±0.1‰ for $\delta^{18}O$ and ±1‰ for $\delta^{2}H$. The following equation explains the δ-notation:

$$\delta^{18}O = \frac{(Rspl - Rstd)}{Rstd} \times 10^{3},$$

Where Rspl is the ratio of the heavy to the light isotope sample and Rstd is the ratio of the heavy to the light isotope standard ($^{18}O/^{16}O$) (Faure, 1998). $\delta^{18}O$ measurements had a precision of 0.2% based on duplicates. $\delta^{2}H$ measurements had a precision of 2.4% based on duplicates.

A T-test was used to determine if groups were statistically different from one another in terms of the various hydrochemical components being examined in this study. For each component the null hypothesis is that there is no difference between the two groups. The alternative hypothesis is that there is a difference between the two groups in question. For this study a probability below the 5% significance level ($p<0.05$) refutes the null hypothesis and confirms the alternative hypothesis that the two groups are different from one another.

Geospatial Analysis

The locations of the sample sites were plotted in ArcMap (ArcGIS 9.2). The map is based on satellite imagery produced by the Advanced Spaceborne Thermal Emission and Reflection Radiometer (ASTER). ASTER acquires high spatial resolution data in 14 bands, from the visible to the thermal infrared wavelengths (NASA JPL, 2010). Bands 1 (520 – 600 nm) and 2 (630 – 690 nm) are in the visible portion of the electromagnetic spectrum and band 3 (760 – 860 nm) is in the near-infrared portion of the electromagnetic spectrum (NASA JPL, 2010). The image used for this map was processed as a combination of bands 1, 2, and 3 and has a resolution of 15m by 15m and an elevation component, a digital elevation model (DEM). The

projection for the ASTER image and DEM is Universal Transverse Mercator (UTM) Zone 18S. The date of this image is August 8, 2009.

Arc Hydro, a tool for ArcGIS, was used to create a representative stream network and define the Quilcayhuanca drainage basin. An ASTER DEM was used to generate a flow direction layer, a flow accumulation layer, a stream definition layer, and a stream segmentation layer. These layers were then used for catchment grid delineation and catchment polygon processing to delineate a group of sub-basin polygons within the Quilcayhuanca watershed. A combination of these sub-basins yielded the total drainage area of the Quilcayhuanca basin and defined the boundary of the basin.

Next, a LiDAR DEM was added to ArcGIS. LiDAR DEMs are produced when an aircraft scatters laser pulses to measure elevations of points on the ground. The LiDAR DEM has a 1 m resolution and a vertical precision of approximately 15 cm (NOAA, 2010). The LiDAR DEM does not cover the entire valley. Notably, portions of Quil-L and Quil-R are missing. The hillshade function in ArcGIS was used to create an image representing the topography of the valley (Figure 2b). With the resolution of this hillshade the major stream channels in the valley were easily observed and then digitized. The hillshade provides additional detailed information about the location of moraines and other types of deposits. It also provides a better spatial perspective for the sampling sites in Quilcayhuanca.

Mixing Model

A simple, two end-member mixing model was created to calculate relative percentages of surface water and groundwater at two sites in Quilcayhuanca valley. The first site, Quil Bel Conf (#19), was chosen because it sits above the pampas of the lower valley which are hypothesized to be potential storage sites for groundwater. The last site, Park Entrance (#24), is

located at the lower end of the pampas. This is the lowest site in the drainage basin shown in Figure 2a. Thus the relative percentages of groundwater and surface water at this site represent the overall mixture of these components exiting the valley as surface water. Average values of different parameters for the groups Quil Streams and groundwater were used as the two end-members. Precipitation was not used as an end member because precipitation is usually at a minimum during the dry season and no precipitation samples were collected from Quilcayhuanca (Mark *et al*., 2005).

Similar to Baraer *et al*. (2009) tracers used had to be conservative, or the value of a particular component at the mixing point had to fall somewhere between the two end members. Additionally, for a tracer to be used it had to meet these criteria at both sites. Average values for each component were calculated with measured values from sites above the site in question. With these requirements in mind the tracers used were conductivity, Ca^{2+}, Mg^{2+}, SO_4^{2-}, Si, and $\delta^{18}O$. The mixing equation used was

$$C_{out} = f_1 C_{Qms} + (1 - f_1) C_{GW}$$

where

f_1 = the unknown fraction of water at the site coming from surface water

$(1-f_1) = f_2$ = the unknown fraction of water at the site coming from groundwater

C_{out} = the average measured concentration of components at the site in question

C_{Qms} = the average measured concentration of components for the group Quil Streams

C_{GW} = the average measured concentration of components for the group groundwater

Results and Discussion

Ions

Calculated charge balances of individual samples varied from 3% to -23% difference. Of the 25 samples, 11 samples had charge balances ranging from -10% to -23% difference. The average percent difference of all the samples was -7.3%. Taken together, these findings suggest that excess anions or insufficient cations exist in most samples. Possibly important missing cations include Al and Mn (Fortner, 2010). The only excess anion to consider is SO_4^{2-}.

The relative average composition of all samples taken in Quilcayhuanca valley was calculated. The abundances of the cations relative to TZ+ are Ca^{2+} (48%), Mg^{2+} (30%), H^+ (12%), Fe^{2+} (6%), Na^+ (4%), K^+ (1%). These relative cation abundances agree well with normal relative abundances in fresh water systems (Hounslow, 1995). The abundances of the anions relative to TZ- are SO_4^{2-} (98%), HCO_3^- (1%), Cl^- (0.5%), F^- (0.5%). These relative anion abundances are unusual in natural settings, but can be explained by sulfide oxidation reactions (Hounslow, 1995). Average ionic compositions were also computed for each of the major groupings: Quil Streams, tributaries, and groundwater. These average compositions are plotted as a bar graph with the average composition of the Rio Santa for comparison (Figure 7). For additional reference, the ionic concentrations and averages for each group can be found in Table 2.

Glacial runoff is usually a dilute Ca^{2+}-HCO_3^-- SO_4^{2-} solution with variable Na^+-Cl^- (Tranter, 2005). Additionally, glacial melt is usually more dilute than global mean river water (Anderson *et al*., 1997). Upon examination of average chemical compositions of some of the major rivers of the world (Faure, 1998), it is clear that Ca^{2+} and Mg^{2+} concentrations from this study are above global averages, while the other major ions (Na^+, K^+, Cl^-, and HCO_3^-) are below

these global river averages. Furthermore, ionic concentrations from this study can be compared with concentrations of major ions in glacial runoff from different regions of the world (Brown, 2002). Concentrations of all the major ions, except Mg^{2+} and SO_4^{2-}, are relatively similar when compared with ranges from other glacial environments. Mg^{2+} and SO_4^{2-} are anomalously high in comparison. Unusually high Mg^{2+} concentrations are likely the result of weathering of common minerals found in granodiorite and tonalite, like amphibole, biotite, and possibly pyroxene. Extremely high SO_4^{2-} concentrations are the result of pyrite oxidation in the shales of the metasedimentary Chicama formation in the upper section of the valley.

Pyrite oxidation, described by the equation below (Faure, 1998), is the driving force of this unusually acidic natural system.

$$FeS_2 + \frac{7}{2}H_2O + \frac{15}{4}O_2 \rightarrow Fe(OH)_3 + 2SO_4^{2-} + 4H^+$$

The oxidation of pyrite can also take place in the absence of O_2 with Fe^{3+} serving as an electron acceptor:

$$FeS_2 + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+$$

Utilizing hydrolysis, sulfide oxidation is a dominant reaction in subglacial and proglacial environments. These reactions provide protons to solution, lowering the pH and allowing for more carbonate dissolution. The oxidation of pyrite preferentially dissolves carbonates, rather than silicates, because the rate of reaction is much faster (Tranter, 2005). Additionally, this reaction can be accelerated by certain bacteria like *Thiobacillus ferrooxidans* (Faure, 1998).

In natural settings, pyrite oxidation usually occurs in debris-rich environments where bedrock is crushed and scoured from past glacial contact (Tranter, 2005). Accordingly in this study, the Chicama formation in the upper valley (Figure 2b with Chicama fm. contact) is exposed and steeply sloped debris piles abound, notably next to the two lakes and in Quil-L.

Thus in the two lakes and Quil-L scoured rocks from the Chicama formation likely slide down steep slopes into the already acidic waters, further continuing the oxidation of pyrite and addition of protons to the surface waters.

Comparisons can be made between sample groups in terms of ionic composition. For instance, there is little variation between Quil Streams and the tributaries group. However, there are major differences between these two groups and groundwater. Groundwater samples were, on average, lower in relative percentages of Mg^{2+}, H^{+}, and SO_4^{2-} and higher in relative percentages of Na^{+}, K^{+}, and HCO_3^{-} (Figure 7). Increased percentages of Na^{+} and K^{+} in groundwater could be explained by cation exchange processes (Hounslow, 1995) while increased percentages of HCO_3^{-} could be explained by increased interactions with trace carbonates along groundwater flow paths or decreased interaction with pyrite and other sulfide minerals which lower the pH and reduce alkalinity.

Another way to view the relative abundances of these ionic compositions is with a Piper diagram which shows the chemical character of water according to the relative concentration of its constituents. The average ionic composition of each group in Quilcayhuanca, the Rio Santa, and the nonglacierized Cordillera Negra were plotted on a Piper diagram (Figure 8). This particular piper plot includes Ca^{2+}, Mg^{2+}, $Na^{+} + K^{+}$ as the apices for the cation ternary and $CO_3^{2-} + HCO_3^{-}$, $SO4_2^{-}$, and Cl^{-} as the apices for the anion ternary. In a Piper diagram the chemical composition of a mixture of two waters lies along a straight line in the central field, which is the union of the cation and anion ternaries. The relative amount of each end-member contributing to a mixture is inversely proportional to the distance along the line from the end member (Piper, 1944).

The Piper diagram (Figure 8), coupled with the bar graph (Figure 7), indicate that surface water and groundwater in Quilcayhuanca differ in terms of ionic composition. Interestingly, groundwater sites resemble the Rio Santa more closely than surface waters from Quilcayhuanca. Furthermore, the average composition of groundwater, the Rio Santa, and the Cordillera Negra all fall on a mixing line, with groundwater from Quilcayhuanca contributing approximately 60% to the Rio Santa and surface waters from the Cordillera Negra contributing approximately 40%. Although groundwater sites from Quilcayhuanca fall on a mixing line with the Rio Santa and the Cordillera Negra, groundwater from Quilcayhuanca alone certainly does not contribute 60% of the dry season discharge to the Rio Santa.

The Cordillera Blanca itself might contribute 60% of dry season discharge to the Rio Santa, similar to what Mark *et al*. (2005) observed, if groundwater in other valleys is similar in ionic composition to the groundwater in Quilcayhuanca or if groundwater in Quilcayhuanca is similar to surface waters in the other valleys. The ionic composition of groundwater in Quilcayhuanca measured in this study is very similar to the average ionic composition of the major tributaries to the Rio Santa measured by Mark *et al* (2005). Those authors estimated that the Cordillera Blanca contributes about 66% of dry season discharge while the Cordillera Negra contributes about 33%.

Field Measurements

Discharge of the principal channel streams increases steadily moving down-valley. The discharge from the Cuchillacocha Lake outflow (#1) in Quil-R was measured to be 0.1 m^3/s, while the highest sampling site in Quil-L, Cayesh Hi (#7), had a discharge of about 0.2 m^3/s. The discharge was measured to be 0.8 m^3/s at the confluence (#19) of Quil-L and Quil-R. Near the end of the valley at the site Park Entrance (#24) the discharge was measured to be 1.2 m^3/s.

Two informative field measurements were pH and specific conductance. The average pH for all sites in Quilcayhuanca was 3.6. The overall range of pH measurements was 2.8 to 7.3. This range shows a stark contrast compared to the normal pH range of 7 – 10 seen in most glacial environments (Tranter, 2005). During the 24 hour sampling period the pH at the site Quil Bel Conf (#19) site varied between 3.3 and 3.7, suggesting an approximate diurnal variation of 0.4. The Quil Streams group (n=14), had an average pH of 3.8 and ranged from pH 3.4 – 5.4. Groundwater samples (n=3) taken from springs averaged pH 6.4 and ranged from pH 6.1 – 7.3. Tributary samples (n=8) had an average pH of 3.4 and ranged from pH 2.8 – 7.1. Table 1 lists pH values by group. The range of pH values by site and grouping is plotted as a bar graph (Figure 3).

Overall the pH's of stream sites in Quil-L, Quil-R, and Quil-M are similar and thus they were considered as one larger group, Quil Streams. Figure 4, a plot of pH versus elevation, shows that pH increases with decreasing elevation. The blue trend line is fit only through the group Quil Streams and excludes site Quilcay (#25) because it is outside of the Quilcayhuanca drainage basin. The trend observed for increasing pH with decreasing elevation for Quil Streams is attributed to the increasing interaction between the surface waters and groundwater-rich pampas moving down-valley. Furthermore, Quil Streams sites in the Quil-M section of the valley should have a higher pH relative to main channel sites in Quil-L and Quil-R because these tributaries are not interacting with the Chicama formation, which is rich in pyrite (Fe_2S) and is thus the main driving force for production of H^+ ions in the valley. Groundwater sites can be thought of as a separate grouping since samples have statistically different (T-test: $p<0.0001$) pH compared to Quil Streams. The groundwater sites do not show a trend with elevation. Tributary

pH values do not show a trend with elevation and have a much greater range than Quil Streams and groundwater.

Specific conductance, a measure of a sample's ability to conduct electricity, is proportional to the number of ions in solution (Schwartz, 2003). The overall average specific conductance for all sites was 251 μS/cm. A large range was observed for these specific conductance measurements (26 – 495 μS/cm). Quil Streams (n=14) had an average specific conductance of 318 μS/cm and ranged from 226 – 495 μS/cm. Tributaries had an average specific conductance of 206 μS/cm and a wide range (53-421 μS/cm). Groundwater sites (n=3) had an average specific conductance of 77 μS/cm and ranged from 26 – 116 μS/cm. Specific conductance of Quil Streams is statistically different (T-test: $p<0.0006$) from groundwater. Igneous and metamorphic rocks contain silicates and alumino-silicate minerals that are slow to react with groundwater that has a nearly neutral pH. When these minerals dominate the mass dissolved in pore water will be relatively small (Schwartz, 2003) and thus conductivity will be lower.

The specific conductance values from all groups were plotted versus elevation (Figure 5). The solid blue significant trend line fit only through Quil Streams, but excluding site Quilcay (#25), shows that specific conductance decreases with decreasing elevation. One way to interpret this relationship is based on stream discharge. Normally in glacial environments, as discharge increases, specific conductance decreases (Anderson *et al*., 2003; Tranter, 2005) because glacial meltwater is usually more dilute than surface water in the proglacial zone. Another way to interpret this relationship is that surface waters are interacting and mixing more with groundwater in the pampas of Quil-M. This interpretation coincides with the interpretation that pH decreases moving down valley because of increasing contributions from groundwater in

the lower portions of the valley. It also noteworthy that the tributaries Jatun Upper Conf (#2), Jatun Mid (#3), and North Waterfall (#21) are all similar to groundwater in terms of pH and specific conductivity (circled on Figure 4 and Figure 5). This suggests one of two things: either the waters are originating from a groundwater source in the upper portion of Quil-R or they are interacting with a different lithology, presumably the intrusive formation which should not yield acidic waters.

During the 24 hour sampling period the values for specific conductance at the site Quil Bel Conf ranged from 349 – 466 μS/cm (Figure 6). From the local time of the first sample (9:30 pm), the specific conductance gradually decreased to its low value at 7:30 am. After 7:30 am the specific conductance gradually increased to its high value at 14:30 (2:30 pm) and then gradually decreased again. With knowledge of the specific conductance variation between surface water and groundwater in the valley one explanation for this diurnal variation might be that surface water, originating mostly from glacial melt, contributes a greater percentage during the daylight hours while groundwater has an increased role during the night (~7 pm – 7am). Anderson *et al*. (2003) showed that discharge of a river in a glacial valley (Kennicott River, Alaska) is inversely proportional to electrical conductivity. However, those measurements were made much closer to the glacier terminus (0.5 km) and in alkaline waters. The sampling site in this study should have a greater solute concentration because streams draining to this site have a much lower pH, presumably favoring mineral dissolution, and a greater distance (~4km from terminus) to interact with minerals in the proglacial zone.

Nutrients

Three nutrients were considered: total P, total N, and Si (Table 4). The average total P for all samples from Quilcayhuanca was 971 ppb P as PO_4^{3-} with values ranging from 0 – 2197

ppb P as PO_4^{3-}. Quil Streams had an average value of 1211 ppb P as PO_4^{3-} with a range of 687 – 1376 ppb P as PO_4^{3-}. Tributaries in the valley had an average value of 738 ppb P as PO_4^{3-} and ranged from 0 – 2197 ppb P as PO_4^{3-}. However this average for tributaries is probably somewhat unrepresentative since four of the samples had values close to or equal to zero, while the other 4 samples had values greater than 1000 ppb P as PO_4^{3-}.

Groundwater sites had an average value of 443 ppb P as PO_4^{3-} and ranged from 9 – 1297 ppb P as PO_4^{3-}. The two springs in the upper portion of the valley had values close to zero while the site Quil Spring (#23) had the maximum value for the group. Total P shows no trend with elevation (Figure 9). It is also noteworthy that groundwater sites, with the exception of Quil Spring and sites possibly originating from groundwater (Jatun Upper Conf (#2), Jatun Mid (#3), and North Waterfall(#21)), all have very low total P values. This observation suggests that total P could be used to distinguish between groundwater and Quil Streams which are statistically different (T-test: $p< 0.003$).

Rocks which are comminuted by intense physical erosion liberate phosphorus. Average crustal rock contains 1,050 ppm of phosphorus usually from sparingly soluble minerals like apatite and from calcium, aluminum, and ferrous phosphates (O'Neil, 1985). In glacial environments, between 1- 23 $\mu g\ P\ g^{-1}$ is present as readily extractable phosphorus on the surface of glacial flour (Hodson *et al*., 2004). This is likely to be an important factor in the dynamics of young, post-glacial ecosystems. Furthermore, P fluxes from glacial environments are likely to respond directly to increased meltwater runoff (Hodson, 2009). In this study total P showed no trend with elevation, contrary to an expected trend of decreasing phosphorus with elevation. This relationship was expected for two reasons. First, scoured phosphate minerals should be the most readily available near the glacier termini and thus measured total P concentrations should

have their highest values at the highest sampling elevations. In older sediments of the lower valley, more of these scoured minerals should have been removed compared to the most recently glacierized terrain in the upper valley. The second reason for this expectation is that plant life in the lower valley should act as a sink, utilizing P for nutritional purposes and growth. In reality, total P values are probably controlled by the pH at the site since groundwater sites usually have the highest pH and lowest Total P.

The average total N for all samples from Quilcayhuanca was 391 ppb N as NO_3^- with values ranging from 161 – 1957 ppb N as NO_3^-. Quil Streams averaged 381 ppb N as NO_3^- and had a range of 161 – 708 ppb N as NO_3^-. Tributaries had an average of 258 ppb N as NO_3^- and a relatively narrow range of 201 – 336 ppb N as NO_3^-. Groundwater samples had an average of 836 ppb N as NO_3^- and a range of 205 – 1957 ppb N as NO_3^-. Two of the groundwater measurements are similar, but the third measurement, J Spring (#12), is very high and results in an unrepresentative average. No trend is observed between total N and elevation (Figure 10). Total N would not be a good method to distinguish between Quil Streams and groundwater since they are not statistically different (T-test: $p< 0.072$).

The primary source for all fixed nitrogen species is nitrogen gas from the atmosphere. Through a process called nitrogen fixation, most plants convert atmospheric nitrogen to organic nitrogen. Dead plants decompose and yield ammonium salts which are converted to nitrate by a process called nitrification (Hounslow, 1995). Snow- and ice melt provide limited quantities of nitrogen, mostly as NO_3^- and NH_4^+ (Tranter, 2005) and it is possible that NH_4^+ is sourced from mica and feldspar dissolution (Holloway *et al*., 1998) and some may originate from oxidation of organic matter. Cattle, horses and sheep which graze in the valley could also contribute to measured total N.

The average Si for all samples was measured to be 9472 ppb Si as SiO_2 with a range of 462 – 13541 ppb Si as SiO_2. The group Quil Streams had an average value of 9274 ppb Si as SiO_2 and a range of 4395 – 10810 ppb Si as SiO_2. Tributaries had an average value of 9041 ppb Si as SiO_2 and 4062 – 10990 ppb Si as SiO_2. Groundwater samples had an average value of 11887 ppb Si as SiO_2 and a range of 9965 – 13541 ppb Si as SiO_2. The samples J Spring (#12) and Quil Spring (#23) have the highest Si concentrations of all the samples from Quilcayhuanca while Cay Spring is close to the overall average. Silica could potentially be used to distinguish between groundwater and surface water samples since groundwater values are significantly different (T-test: $p < 0.024$) from Quil Streams. Si concentrations increase down valley for Quil Streams (Figure 11). However, this trend is not quite statistically significant at the 5% significance level.

Silica in most low-temperature natural waters is derived from silicate weathering (Hounslow, 1995). In proglacial environments carbonate dissolution and sulfide oxidation reactions dominate initially, but these minerals become exhausted as silicate weathering increases. Colonization of the proglacial zone by plants further increases the rate of chemical weathering of silicates (Anderson *et al*., 2000). These observations coincide well with the measured concentrations of Si and how they vary with elevation in this study. Presumably the oldest glacial deposits are in the lower portions of the valley and these deposits have been interacting with naturally acidic waters for quite some time. As a result, carbonate and sulfide minerals in these lower, older sediment portions of the valley have probably been exhausted leading to increased silicate weathering in these areas.

Isotopes

Two isotopes, $\delta^{18}O$ and $\delta^{2}H$, were measured and deuterium excess was calculated for the samples from Quilcayhuanca valley (Table 6). The average $\delta^{18}O$ for the entire valley was -16.7‰ with a range of -17.8 to -14.4‰. For Quil Streams the average was -16.9‰ with a range of -17.8 to -16.3‰. Tributaries had an average value of -16.6‰ with a range of -17.6 to -14.4‰. Groundwater samples had an average value of -16.0‰ with a range of -17.5 to -15.3‰. J Spring (#12) and Quil Spring (#23) have identical values while Cay Spring (#15) is unexpectedly low (depleted). One possible explanation for this is that Cay Spring has a shorter residence time or flow path than the other two springs, meaning that there is less time to evaporate compared to other groundwater. As a result, the surface water that initially entered this spring does not change as much compared to the other two sites. This theory is supported by measurements of conductivity. Cay Spring has the lowest conductivity of the three groundwater sites. With a longer residence time, the quantity of mass dissolved in groundwater increases (Schwartz, 2003) and thus so does conductivity.

A plot of $\delta^{18}O$ versus elevation shows an elevation effect of -0.155 ‰ per 100 m of elevation rise (Figure 12). This elevation effect is approximately two times as large as the elevation effect observed for the nonglacierized Cordillera Negra (-0.07‰ per 100 m) by Mark *et al*. (2007) from 2004-2006. Although it is difficult to quantify the amount of glacial meltwater in the surface waters of Quilcayhuanca, this comparison shows that meltwaters play a significant role during the dry season.

The average $\delta^{2}H$ for the entire valley was -126‰ with a range of -134 to -110‰. For Quil Streams the average was -126‰ with a range of -134 to -120‰. Tributaries had an average value of -126‰ with a range of -134 to -110‰. Groundwater samples had an average of -122‰

with a range of -134 to -115‰. A plot of $\delta^{18}O$ versus $\delta^{2}H$ depicts the local meteoric water line for Quilcayhuanca valley (Figure 13). The local meteoric water line falls below the global meteoric water line (MWL). This result is usually attributed to evaporative enrichment, which is fitting in this case because samples were taken during the dry season. A similar effect for 2004 – 2006 was observed by Mark *et al*. (2007).

The average $\delta^{18}O$ and $\delta^{2}H$ of Quilcayhuanca, the Rio Santa, and the Cordillera Negra were plotted with error bars (1 standard deviation) to represent mixing of these groups. As expected, the waters from Quilcayhuanca have the most negative values of $\delta^{18}O$ and $\delta^{2}H$ resulting from glacial melt and runoff derived from higher elevation precipitation. Based on average isotopic values of the Rio Santa and Cordillera Negra (Table 7) and the assumption that the site Quilcay (~2 km from the Rio Santa) is representative of the Cordillera Blanca, this mixing model suggests that between 27% ($\delta^{18}O$) and 38% ($\delta^{2}H$) of the water in the Rio Santa is derived from the Cordillera Blanca. This calculation is a crude estimate of relative contributions to the Rio Santa since discharge and precipitation are not included and one valley is used to represent the entire Cordillera Blanca. Nevertheless, it is a useful exercise and provides the foundation for further more detailed studies.

Isotopically, one question remains to be answered: why are the groundwater samples statistically different (T-test: $p<0.037$) from surface waters samples in terms of $\delta^{18}O$? And more importantly, why do they have, on average, more positive values? Normally $\delta^{18}O$ of shallow groundwater and $\delta^{18}O$ of local precipitation are approximately the same (Clark and Fritz, 1997). However, in the Cordillera Blanca most precipitation falls in the wet season and is usually more depleted than the most negative value measured in Quilcayhuanca in this study. Thus shallow groundwater, at least in Quilcayhuanca, is not a mirror image of wet season precipitation. Along

the same lines, dry season precipitation should not be a major factor in determining the isotopic composition of groundwater since precipitation during this time is usually at a minimum. The most likely explanation for this observation is evaporation of shallow groundwater.

Mixing Model

An average of the individual mixing models provides an estimate that the site Quil Bel Conf is 76% surface water and 24% groundwater with a standard deviation of ±0.16% (Table 8). The site Park Entrance is estimated to be 66% surface water and 34% groundwater with a standard deviation of ±0.12%. These two sites are not statistically different (T-test: $p<0.27$) in terms of their relative contribution from surface water and groundwater. In general, however, it appears that groundwater is a slightly larger component at the last site after the streams pass through the prospective groundwater storage sites known as pampas.

A similar, but more complex, model was applied to the 7% glacierized Querococha basin of the Cordillera Blanca by Baraer *et al*. (2009). The authors report that groundwater is the dominant contributor to Querococha surface waters during the dry season. The authors note that the relative contribution from groundwater is variable, ranging from 18 to 74%, but that proglacial groundwater contributions are a key component of the dry season hydrologic system in this valley and possibly the rest of the Cordillera Blanca. Therefore the groundwater component in these glacial environments should not be ignored in future studies quantifying or modeling water resources (Baraer *et al*., 2009).

Conclusions and Future Work

1. Pyrite oxidation is the dominant reaction in the proglacial zone of Quilcayhuanca. This reaction adds protons to solution and lowers the pH to below 4 at many sites. As a result of such

a low pH there is almost no alkalinity and igneous rocks are readily weathered, resulting in high solute concentrations. The sampling group Quil Streams is characterized by Ca^{2+}, Mg^{2+}, and SO_4^{2-} which are consistent with the mapped lithology of granodiorite/tonalite and the metasedimentary Chicama formation.

2. Hydrochemical parameters show trends with elevation. pH decreases with elevation but specific conductance increases. Both of these trends support the idea that surface waters are potentially mixing more with groundwater in lower portions of the valley. Total P and total N of Quil Streams sites show no trend with elevation. Si concentrations increase with decreasing elevation because sulfide and carbonate minerals have been more exhausted at lower elevations. An elevation effect of -0.155‰ per 100 m rise in elevation was observed for $\delta^{18}O$ which is nearly twice the published elevation effect of the nonglacierized Cordillera Negra. This signifies that glacial melt is a large reason $\delta^{18}O$ in Quilcayhuanca is much more negative than would normally be expected at a given elevation.

3. Surface waters and groundwater in Quilcayhuanca are geochemically different in several ways. pH is lower for surface waters as a result of increased interaction with abundant pyrite. Specific conductance is lower for groundwater samples due to their near neutral pH and decreased dissolution potential. Groundwater in this valley had considerably higher relative percentages of Na^+, K^+, and HCO_3^- as a result of cation exchange processes and dissolution of trace carbonates. Surface waters had considerably higher relative percentages of Mg^{2+}, Fe^{2+}, H^+, and SO_4^{2-} relative to groundwater. Groundwater usually has almost no total P and higher concentrations of Si, relative to surface waters. $\delta^{18}O$ and δ^2H of groundwater are, on average, more positive than $\delta^{18}O$ and δ^2H of surface waters. These differences provide ways to

differentiate between groundwater and surface water. These differentiations aid in the selection of parameters for mixing models.

4. Using a simple, two end-member mixing model, the surface waters leaving the valley at the lowest site in the drainage basin were calculated to be a mixture of approximately two-thirds surface water (mostly glacial melt) and one-third groundwater. Pampas could potentially increase the relative contribution from groundwater in the lower valley. Groundwater is clearly an important component of the dry season hydrologic budget.

This case study of one glacial valley in the tropical Cordillera Blanca sought to examine the geochemistry with the hope of shedding new light on the hydrochemical variation in glacial environments. In future studies it would be very interesting and informative to calculate weathering rates in this strongly acidic glacial environment. Furthermore, the role between nutrients and the biology of the valley could be explored in more detail. Isotopic variations in glacial environments are still somewhat mysterious, especially for ice and groundwater samples. Future work could include a study related to the isotopic fractionation of melting glacial ice. Finally, more groundwater samples, and possibly ages, are needed to hydrochemically characterize this important dry season water resource.

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Tables

Table 1 – Quilcayhuanca Field Measurements by Group

Site Name	Subgroup	Site #	Elevation m.a.s.l.	pH	Conductivity µS/cm
Cuchillacocha out	Quil-R	1	4624	3.4	478
Tulpacocha	Quil-R	4	4290	3.4*	-
Lower Lake (Tupla) Out	Quil-R	5	4282	3.4	495
Jatun	Quil-R	10	4178	3.5	390
Cuchi Conf	Quil-R	13	4148	3.8	304
Tulp Low	Quil-R	14	4148	3.8	281
V2 Ab Pacsa	Quil-R	16	4056	3.9	258
Tulp Ab Conf	Quil-R	17	4034	4.1	259
Quil-R Avg.			**4220**	**3.6**	**352**
Cay Hi	Quil-L	7	4232	3.8	226
Cay Ab Conf	Quil-L	18	4032	4.6	391
Quil-L Avg.			**4132**	**4.1**	**309**
Quil Bel Conf	Quil-M	19	4031	4.3	296
Casa de Agua	Quil-M	22	3917	3.7	293
Park Entrance	Quil-M	24	3835	4.1	228
Quilcay	Quil-M	25	3109	5.4	241
Quil-M Avg.			**3723**	**4.1**	**265**
Quil Streams Avg.				**3.8**	**318**
Jatun Upper Conf	Tribs	2	4564	6.3	176
Jatun Mid	Tribs	3	4292	6.4	133
Cay L1	Tribs	6	4236	3.2	421
Cay Red	Tribs	8	4216	3.0	314
Cay L2	Tribs	9	4180	4.5	242
Cay L3	Tribs	11	4177	2.8	130
South Waterfall	Tribs	20	3995	3.8	179
North Waterfall	Tribs	21	3994	7.1	53
Tribs Avg.			**4207**	**3.4**	**206**
J Spring	GW	12	4162	6.8	88
Cay Spg	GW	15	4109	6.1	26
Quil Spring	GW	23	3878	7.3	116
Avg. Groundwater			**4050**	**6.4**	**77**

*July 2008 measurement; - indicates no measurement

Table 2 – Quilcayhuanca Ion Concentrations by Group

Site Name	Subgroup	Site #	Elevation m.a.s.l.	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	Fe^{2+}	H^{+}	F^{-}	Cl^{-}	HCO_3^{-}	SO_4^{2-}
				meq/L									
Cuchillacocha out	Quil-R	1	4624	1.59	1.12	0.06	0.02	0.16	0.42	0.01	0.01	0.00	3.15
Tulpacocha	Quil-R	4	4290	-	-	-	-	-	-	-	-	-	-
Lower Lake (Tupla) Out	Quil-R	5	4282	1.49	1.08	0.07	0.02	0.08	0.44	0.01	0.01	0.00	3.08
Jatun	Quil-R	10	4178	1.39	0.83	0.07	0.02	0.06	0.33	0.01	0.01	0.00	2.70
Cuchi Conf	Quil-R	13	4148	1.11	0.66	0.09	0.02	0.04	0.16	0.01	0.01	0.00	2.23
Tulpa Low	Quil-R	14	4148	0.65	0.57	0.04	0.02	0.03	0.17	0.01	0.01	0.00	2.04
V2 Ab Pacsa	Quil-R	16	4056	0.77	0.55	0.06	0.02	0.02	0.13	0.01	0.01	0.00	2.00
Tulp Ab Conf	Quil-R	17	4034	0.77	0.56	0.06	0.02	0.02	0.09	0.01	0.02	0.00	2.01
Quil-R Avg.			**4220**	**1.11**	**0.77**	**0.07**	**0.02**	**0.06**	**0.25**	**0.01**	**0.01**	**0.00**	**2.46**
Cay Hi	Quil-L	7	4232	0.78	0.38	0.03	0.01	0.02	0.15	0.00	0.01	0.00	1.44
Cay Ab Conf	Quil-L	18	4032	1.24	0.78	0.04	0.01	0.35	0.02	0.01	0.01	0.00	2.85
Quil-L Avg.			**4132**	**1.01**	**0.58**	**0.03**	**0.01**	**0.18**	**0.09**	**0.01**	**0.01**	**0.00**	**2.15**
Quil Bel Conf	Quil-M	19	4031	0.88	0.58	0.06	0.02	0.09	0.05	0.01	0.01	0.00	2.18
Casa de Agua	Quil-M	22	3917	0.85	0.58	0.06	0.02	0.07	0.19	0.01	0.02	0.00	2.14
Park Entrance	Quil-M	24	3835	0.68	0.50	0.09	0.02	0.02	0.08	0.01	0.02	0.00	1.85
Quilcay	Quil-M	25	3109	0.94	0.37	0.10	0.03	0.00	0.00	0.00	0.06	0.00	1.48
Quil-M Avg.			**3723**	**0.84**	**0.51**	**0.08**	**0.02**	**0.04**	**0.08**	**0.01**	**0.03**	**0.00**	**1.91**
Quil Streams Avg.			**4065**	**1.01**	**0.66**	**0.06**	**0.02**	**0.07**	**0.17**	**0.01**	**0.02**	**0.00**	**2.24**
Jatun Upper Conf	Tribs	2	4564	1.24	0.30	0.07	0.02	0.00	0.00	0.01	0.01	0.12	1.48
Jatun Mid	Tribs	3	4292	0.68	0.22	0.09	0.03	0.00	0.00	0.01	0.01	0.00	1.09
Cay L1	Tribs	6	4236	0.48	0.49	0.01	0.00	0.05	0.62	0.01	0.01	0.00	2.04
Cay Red	Tribs	8	4216	4.09	2.47	0.12	0.02	1.07	1.00	0.04	0.00	0.00	11.69
Cay L2	Tribs	9	4180	0.57	0.46	0.02	0.01	0.00	0.03	0.01	0.01	0.00	1.71
Cay L3	Tribs	11	4177	0.82	1.15	0.07	0.01	0.61	1.58	0.05	0.01	0.00	5.19
South Waterfall	Tribs	20	3995	0.38	0.26	0.05	0.01	0.01	0.17	0.01	0.01	0.00	1.20
North Waterfall	Tribs	21	3994	0.34	0.03	0.05	0.02	0.00	0.00	0.01	0.01	0.23	0.19
Tribs Avg.			**4207**	**1.07**	**0.67**	**0.06**	**0.01**	**0.22**	**0.43**	**0.02**	**0.01**	**0.04**	**3.07**

J Spring	GW	12	4162	0.29	0.10	0.15	0.03	0.00	0.00	0.00	0.01	0.22	0.34
Cay Spg	GW	15	4109	0.14	0.02	0.05	0.01	0.00	0.00	0.01	0.00	0.08	0.13
Quil Spring	GW	23	3878	0.35	0.17	0.16	0.05	0.09	0.00	0.01	0.01	0.12	0.67
Avg. Groundwater			**4050**	**0.26**	**0.10**	**0.12**	**0.03**	**0.03**	**0.00**	**0.01**	**0.01**	**0.14**	**0.38**

- indicates no measurement

Table 3 – Rio Santa and Cordillera Negra Ion Concentrations

Site Name	Subgroup	Site #	Elevation m.a.s.l.	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	Fe^{2+}	H^{+}	F^{-}	Cl^{-}	HCO_3^{-}	SO_4^{2-}
				meq/L									
Jangas	Santa		2807	-	-	-	-	-	-	-	-	-	-
Santa 1	Santa		3800	1.43	0.26	0.52	0.06	0.01	-	0.00	0.32	1.62	0.33
Santa 2	Santa		3462	1.07	0.45	0.67	0.08	0.00	-	0.01	0.29	0.67	1.30
Santa Low	Santa		2000	2.18	0.57	0.71	0.09	0.00	-	0.01	0.56	1.39	1.59
Conococha	Santa		4020	0.56	0.13	0.36	0.06	0.01	-	0.00	0.02	0.00	2.05
Santa Tica	Santa		3433	0.95	0.28	0.29	0.05	0.01	-	0.00	0.01	1.54	0.03
La Recreta	Santa		3990	1.49	0.24	0.42	0.05	0.01	-	0.00	0.00	1.60	0.59
Pteucushacu	Santa		3930	1.36	0.22	0.44	0.05	0.00	-	0.00	0.03	0.48	1.57
Santa Catac	Santa		3547	1.25	0.37	0.38	0.06	0.00	-	0.00	0.22	1.07	0.77
Rio Santa Avg.	Santa		**3443**	**1.29**	**0.31**	**0.47**	**0.06**	**0.00**	**-**	**0.00**	**0.18**	**1.05**	**1.03**
Negra 1	Negra		4004	0.16	0.09	0.08	0.02	0.00	-	0.00	0.23	0.00	0.57
Negra 2	Negra		3973	2.32	0.61	0.41	0.03	0.00	-	0.01	0.02	1.96	1.39
Negra Anta	Negra		2765	2.16	1.23	0.66	0.07	0.00	-	0.01	0.10	3.42	0.58
Negra Low	Negra		2038	2.02	0.32	1.26	0.04	0.00	-	0.00	0.01	3.49	0.13
Cord. Negra Avg.	Negra		**3195**	**1.66**	**0.56**	**0.60**	**0.04**	**0.00**	**-**	**0.01**	**0.09**	**2.22**	**0.67**

- indicates no measurement

Table 4 – Nutrient Concentrations for Quilcayhuanca by Group

Site Name	Subgroup	Site #	Elevation m.a.s.l.	Total P ppb P as PO_4^{3-}	Total N ppb N as NO_3^-	Si ppb Si as SiO_2
Cuchillacocha out	Quil-R	1	4624	1343	389	7954
Tulpacocha	Quil-R	4	4290	1291	202	8248
Lower Lake (Tupla) Out	Quil-R	5	4282	1335	364	8919
Jatun	Quil-R	10	4178	1376	401	9411
Cuchi Conf	Quil-R	13	4148	1179	605	10810
Tulpa Low	Quil-R	14	4148	1289	278	8990
V2 Ab Pacsa	Quil-R	16	4056	1342	384	10382
Tulp Ab Conf	Quil-R	17	4034	1307	369	10260
Quil-R Avg.			**4220**	**1308**	**374**	**9372**
Cay Hi	Quil-L	7	4232	687	161	4395
Cay Ab Conf	Quil-L	18	4032	1352	364	8400
Quil-L Avg.			**4132**	**1020**	**263**	**6397**
Quil Bel Conf	Quil-M	19	4031	1337	274	10059
Casa de Agua	Quil-M	22	3917	1297	345	9968
Park Entrance	Quil-M	24	3835	1211	308	10505
Quilcay	Quil-M	25	3109	692	708	10504
Quil-M Avg.			**3723**	**1134**	**409**	**10259**
Quil Streams Avg.			**4065**	**1211**	**381**	**9274**
Jatun Upper Conf	Tribs	2	4564	30	232	9033
Jatun Mid	Tribs	3	4292	22	256	10815
Cay L1	Tribs	6	4236	1273	336	4062
Cay Red	Tribs	8	4216	2197	245	10990
Cay L2	Tribs	9	4180	1080	330	7988
Cay L3	Tribs	11	4177	1301	233	10814
South Waterfall	Tribs	20	3995	0	234	10056
North Waterfall	Tribs	21	3994	0	201	8574
Tribs Avg.			**4207**	**738**	**258**	**9041**

J Spring	GW	12	4162	23	1957	12153
Cay Spg	GW	15	4109	9	205	9965
Quil Spring	GW	23	3878	1297	345	13541
Avg. Groundwater			**4050**	**443**	**836**	**11887**

0 ppb is equivalent to below detection limit

Table 5 – Nutrient Concentrations of the Rio Santa and Cordillera Negra

Site Name	Subgroup	Site #	Elevation	Total P	Total N	Si
			m.a.s.l.	ppb P as PO_4^{3-}	ppb N as NO_3^-	ppb Si as SiO_2
Jangas	Santa		2807	943	1919	11460
Santa 1	Santa		3800	1164	488	10812
Santa 2	Santa		3462	1166	642	11207
Santa Low	Santa		2000	1407	2127	12162
Conococha	Santa		4020	78	909	484
Santa Tica	Santa		3433	1155	544	10504
La Recreta	Santa		3990	-	-	-
Pteucushacu	Santa		3930	825	351	10992
Santa Catac	Santa		3547	1195	347	9966
Rio Santa Avg.			**3443**	**999**	**772**	**9447**
Negra 1	Negra		4004	0	305	9796
Negra 2	Negra		3973	13	231	13541
Negra Anta	Negra		2765	1210	1153	11758
Negra Low	Negra		2038	643	815	13542
Cord. Negra Avg.			**3195**	**467**	**626**	**12159**

- indicates no measurement

Table 6 – Stable Isotope for Quilcayhuanca by Group

Site Name	Subgroup	Site #	Elevation m.a.s.l.	$\delta^{18}O$ ‰	$\delta^{2}H$ ‰	D-excess ‰
Cuchillacocha out	Quil-R	1	4624	-17.8	-134	7.9
Tulpacocha	Quil-R	4	4290	-17.0	-126	9.9
Lower Lake (Tupla) Out	Quil-R	5	4282	-17.4	-127	11.9
Jatun	Quil-R	10	4178	-17.4	-129	10.2
Cuchi Conf	Quil-R	13	4148	-17.0	-129	7.1
Tulpa Low	Quil-R	14	4148	-17.0	-128	7.9
V2 Ab Pacsa	Quil-R	16	4056	-16.8	-123	10.9
Tulp Ab Conf	Quil-R	17	4034	-16.8	-126	8.5
Quil-R Avg.			**4220**	**-17.1**	**-128**	**9.3**
Cay Hi	Quil-L	7	4232	-16.5	-120	11.9
Cay Ab Conf	Quil-L	18	4032	-16.7	-126	8.0
Quil-L Avg.			**4132**	**-16.6**	**-123**	**9.9**
Quil Bel Conf	Quil-M	19	4031	-16.9	-126	8.8
Casa de Agua	Quil-M	22	3917	-16.6	-126	6.7
Park Entrance	Quil-M	24	3835	-16.5	-126	6.0
Quilcay	Quil-M	25	3109	-16.3	-124	6.9
Quil-M Avg.			**3723**	**-16.6**	**-126**	**7.1**
Quil Streams Avg.			**4065**	**-16.9**	**-126**	**8.6**
Jatun Upper Conf	Tribs	2	4564	-17.6	-132	8.7
Jatun Mid	Tribs	3	4292	-16.6	-127	5.8
Cay L1	Tribs	6	4236	-16.8	-125	9.5
Cay Red	Tribs	8	4216	-14.4	-110	4.9
Cay L2	Tribs	9	4180	-16.8	-125	9.5
Cay L3	Tribs	11	4177	-16.9	-127	7.7
South Waterfall	Tribs	20	3995	-17.8	-134	8.4
North Waterfall	Tribs	21	3994	-16.3	-126	4.5
Tribs Avg.			**4207**	**-16.6**	**-126**	**7.4**

J Spring	GW	12	4162	-15.3	-118	4.6
Cay Spg	GW	15	4109	-17.5	-134	5.7
Quil Spring	GW	23	3878	-15.3	-115	7.7
Avg. Groundwater			**4050**	**-16.0**	**-122**	**6.0**

Table 7 – Stable Isotope Results for the Rio Santa and Cordillera Negra

Site Name	Subgroup	Site #	Elevation m.a.s.l.	$\delta^{18}O$ ‰	$\delta^{2}H$ ‰	D-excess ‰
Jangas	Santa		2807	-15.1	-118	3.0
Santa 1	Santa		3800	-12.6	-105	-4.1
Santa 2	Santa		3462	-14.9	-112	7.1
Santa Low	Santa		2000	-14.8	-114	5.0
Conococha	Santa		4020	-10.4	-96	-12.8
Santa Tica	Santa		3433	-14.7	-115	2.7
La Recreta	Santa		3990	-16.2	-125	4.5
Pteucushacu	Santa		3930	-13.1	-108	-2.7
Santa Catac	Santa		3547	-14.6	-113	3.6
Rio Santa Avg.			**3443**	**-13.9**	**-111**	**0.4**
Negra 1	Negra		4004	-13.8	-110	0.3
Negra 2	Negra		3973	-13.7	-115	-6.0
Negra Anta	Negra		2765	-12.1	-96	1.1
Negra Low	Negra		2038	-12.3	-92	6.1
Cord. Negra Avg.			**3195**	**-13.0**	**-103**	**0.4**

Table 8 – Results of Mixing Model with Overall Averages and Standard Deviations for f_1 and f_2

Quil Bel Conf		Conduc. µS/cm	Ca2+ meq/L	Mg2+ meq/L	SO42- meq/L	Si ppb Si as SiO_2	δ18O ‰		
	Cqms	342	1.09	0.73	2.39	8777	-17.0		
	Cgw	57	0.21	0.06	0.24	11059	-16.4		
	Cout	296	0.88	0.58	2.18	10059	-16.9		
								Average	**1 Stdev**
Surface Water	f1	0.84	0.76	0.78	0.90	0.44	0.83	**0.76**	**0.16**
Groundwater	f2	0.16	0.24	0.22	0.10	0.56	0.17	**0.24**	
Park Entrance		Conduc. µS/cm	Ca2+ meq/L	Mg2+ meq/L	SO42- Meq/L	Si ppb Si as SiO_2	δ18O ‰		
	Cqms	300	0.94	0.61	2.18	9186	-16.8		
	Ggw	77	0.26	0.10	0.38	11887	-16.04		
	Cout	228	0.68	0.50	1.85	10505	-16.5		
								Average	**1 Stdev**
Surface Water	f1	0.68	0.63	0.78	0.82	0.51	0.55	**0.66**	**0.12**
Groundwater	f2	0.32	0.37	0.22	0.18	0.49	0.45	**0.34**	

Figures

Figure 1 – Map of Cordillera Blanca (modified from Mark and McKenzie, 2007)
The red box shows the location of the Quilcayhuanca drainage basin relative to the Cordillera Blanca and the Rio Santa.

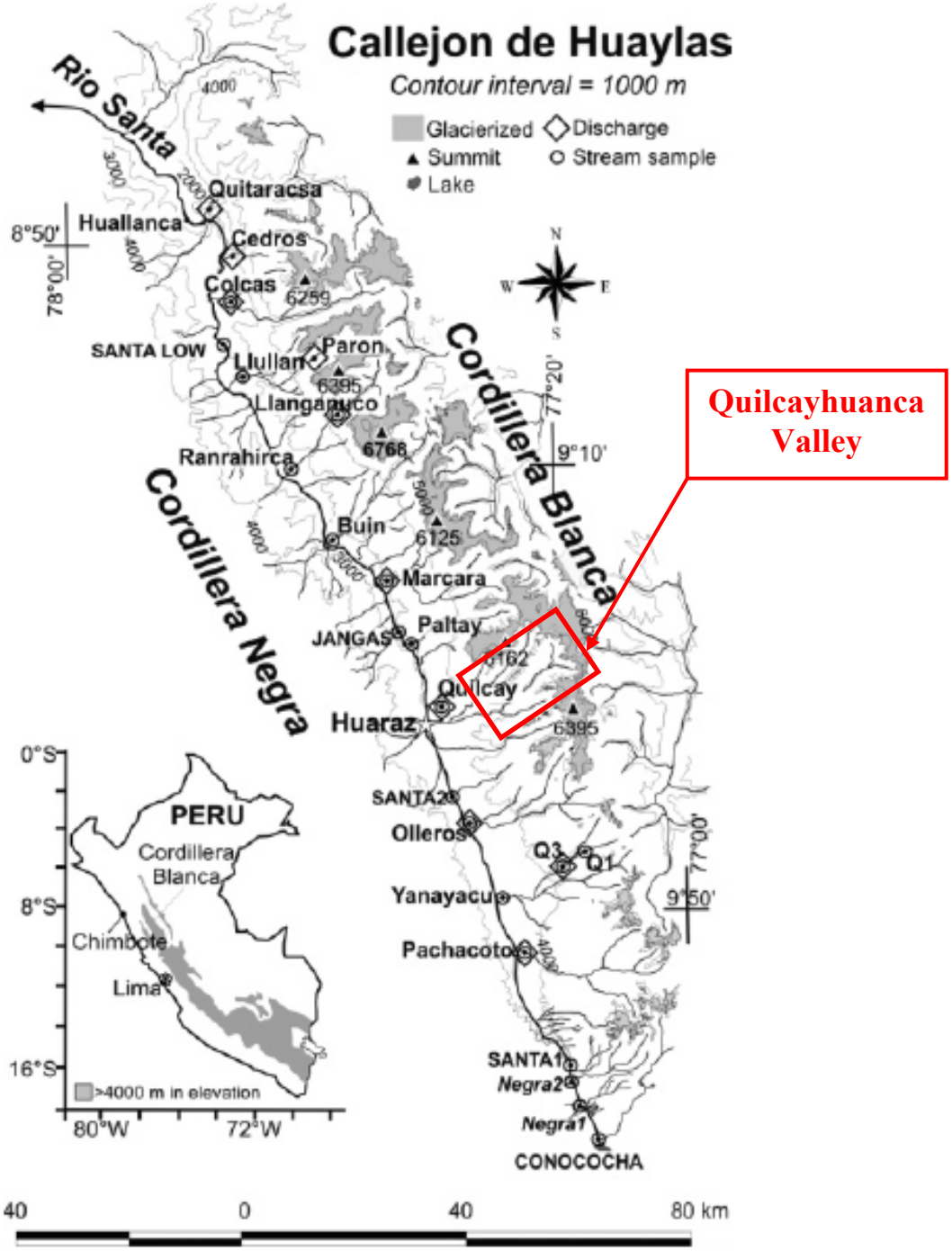

Figure 2a – Geologic Map of Quilcayhuanca Drainage Basin with Sampling Site Locations
This geologic map shows the major formations of the Quilcayhuanca drainage basin. Glaciers and lakes are also mapped. Sampling locations are plotted with symbols appropriate to their grouping. Labeled ovals surround the three sections of the valley: Quil-L, Quil-R, and Quil-M.

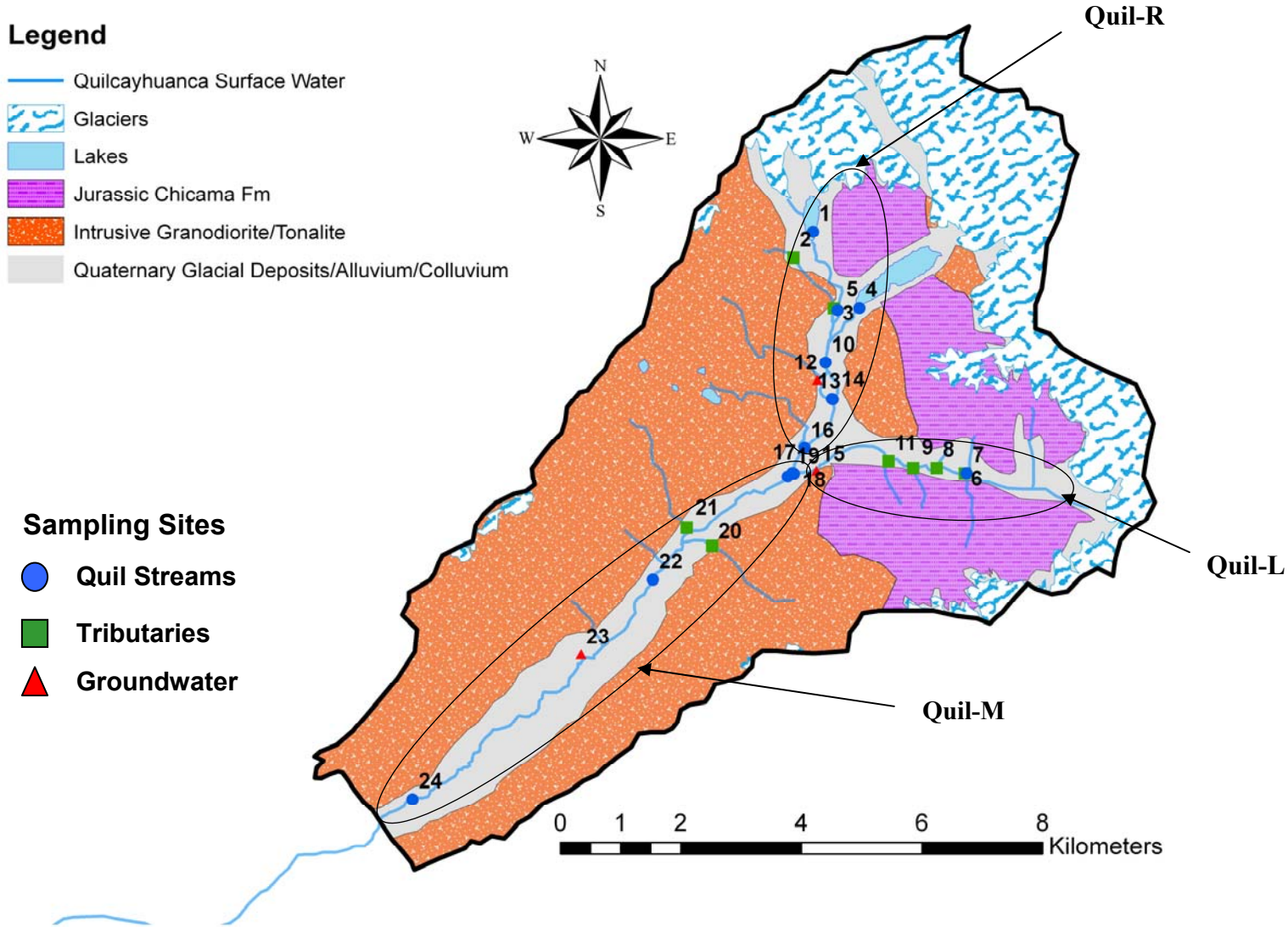

Figure 2b – LiDAR Hillshade of the Upper Portion of Quilcayhuanca Valley with Sampling Sites and Chicama Contact
This LiDAR hillshade focuses on the upper part of Quilcayhuanca valley. Sampling locations are plotted with symbols appropriate to their grouping. The Chicama formation contact (thick purple line) was transferred from the geologic map. Blank, light-grey areas are zones where there is no LiDAR coverage available.

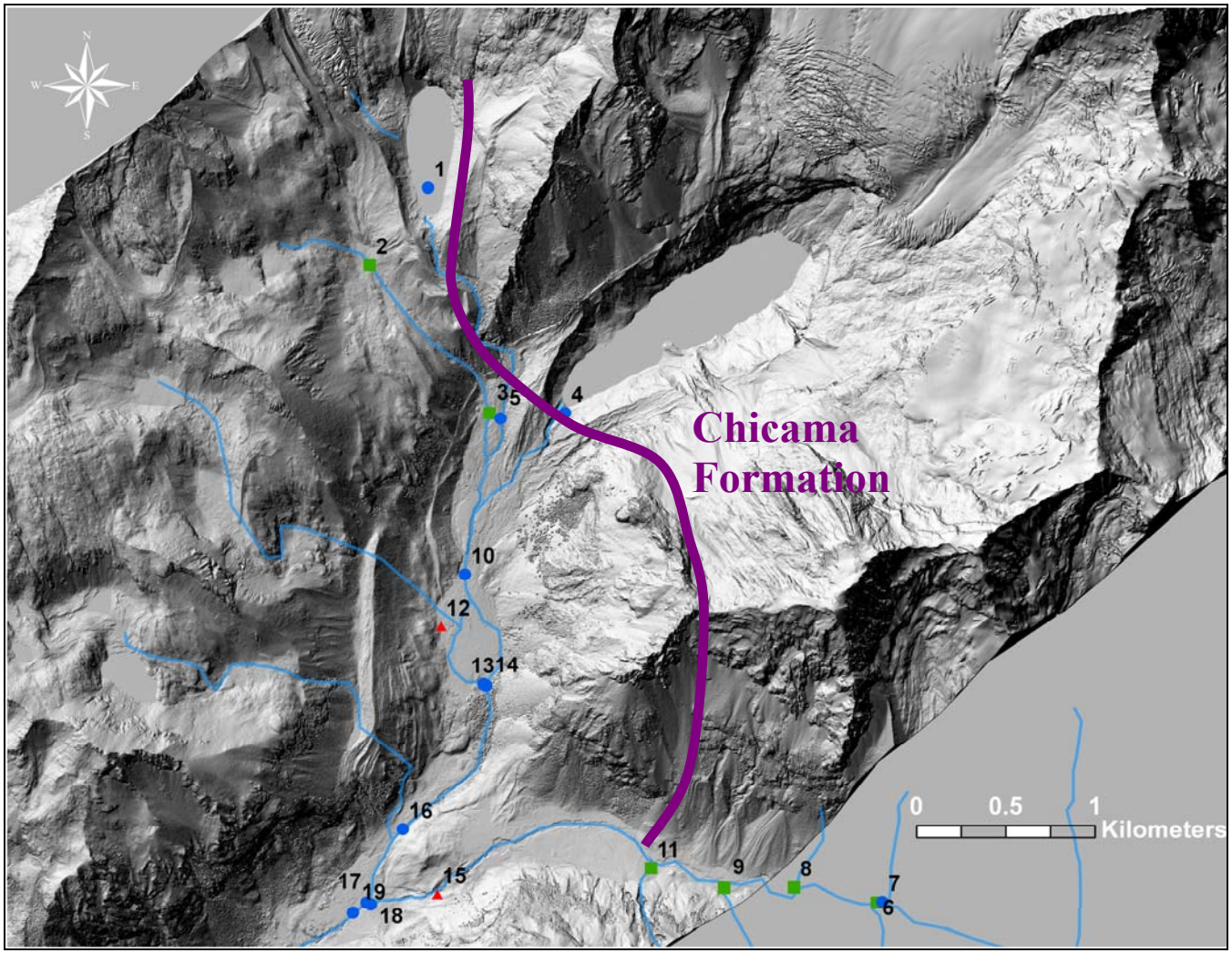

Figure 3 – pH values by Site and Grouping
Measured pH values are displayed within their respective group. Quil Streams, outlined by a blue box, is subdivided into Quil-R, Quil-L, and Quil-M. The tributaries group is outlined by a green box, while the groundwater group is outlined by a red box. Tributaries have the most variation while groundwater samples have the highest overall pH.

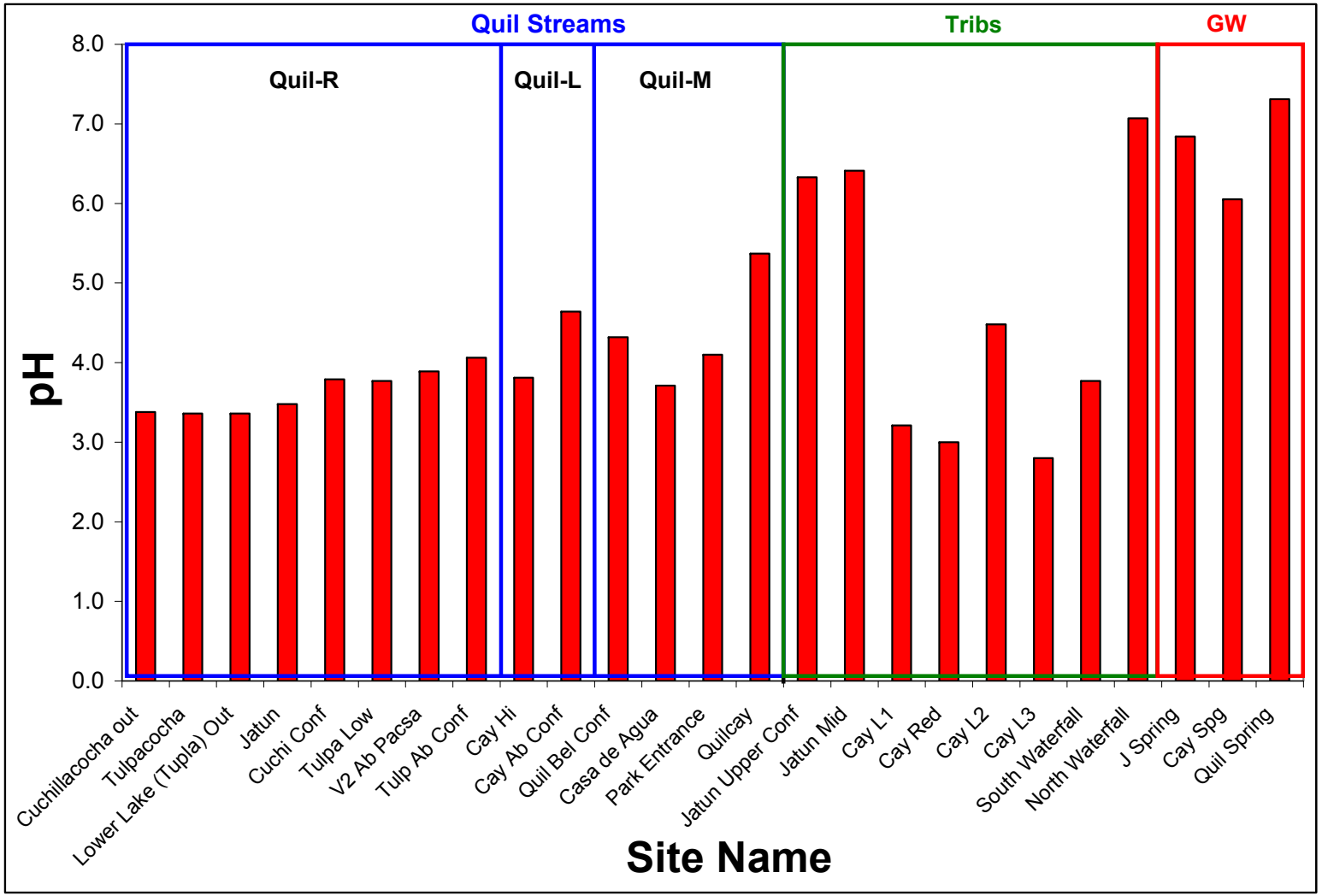

Figure 4 – pH versus Elevation for Sampling Sites in Quilcayhuanca
Groundwater sites and tributaries #2, #3, and #21 have the highest pH. A trend line fit only through Quil Streams, but excluding Quilcay (#25) because it is outside of the drainage basin, shows that pH decreases with decreasing elevation. The solid blue line indicates that the trend is significant at the 5% significance level.

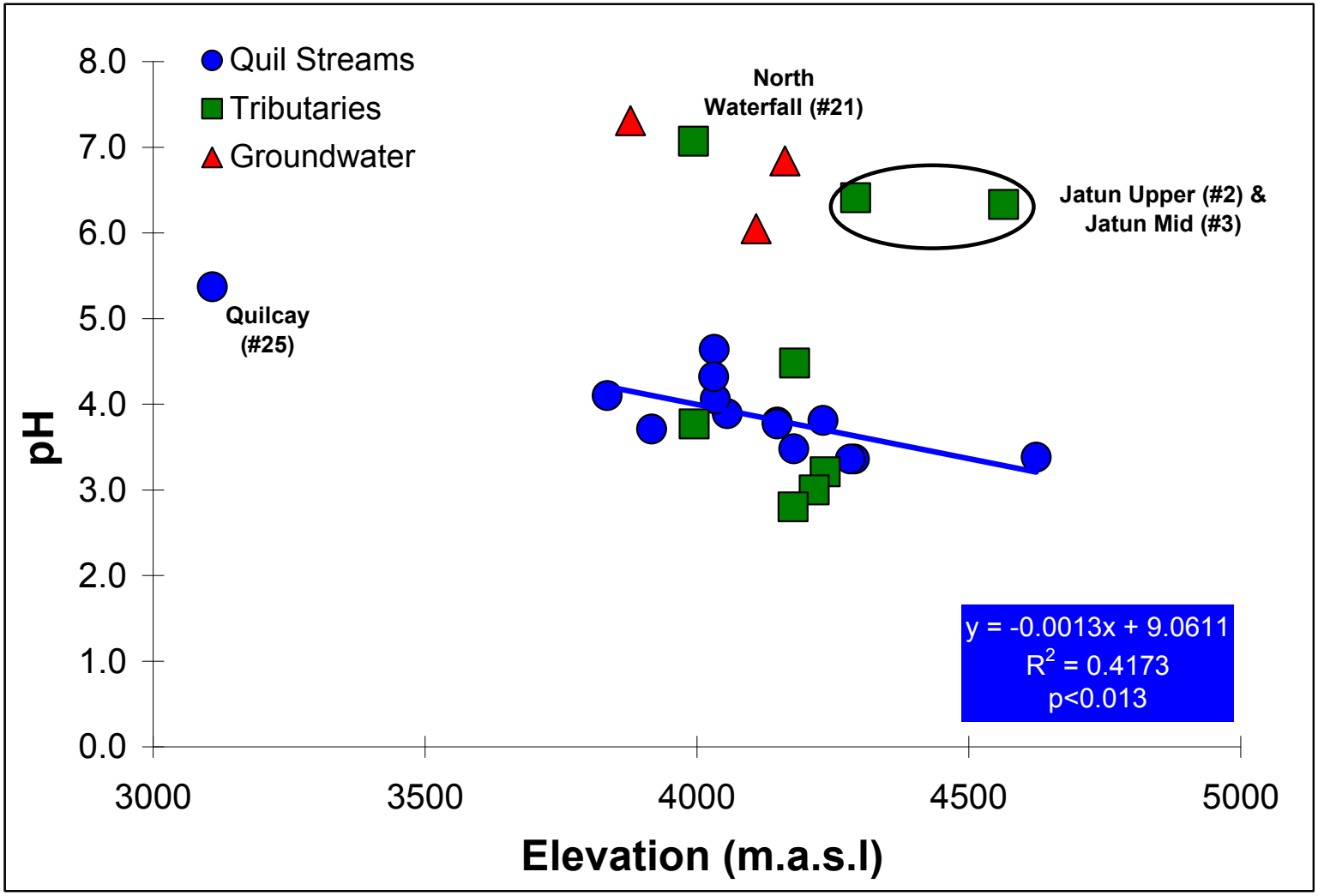

Figure 5 – Specific Conductance versus Elevation for Sampling Sites in Quilcayhuanca
Cuchillacocha, a major lake in Quil-R, has the highest specific conductance while samples with a higher pH (groundwater samples and sites #2, #3, and #21) have the lowest specific conductance. A trend line fit only through Quil Streams, but excluding Quilcay (#25) because it is outside of the drainage basin, shows that specific conductance decreases with decreasing elevation. The solid blue line indicates that the trend is significant at the 5% significance level.

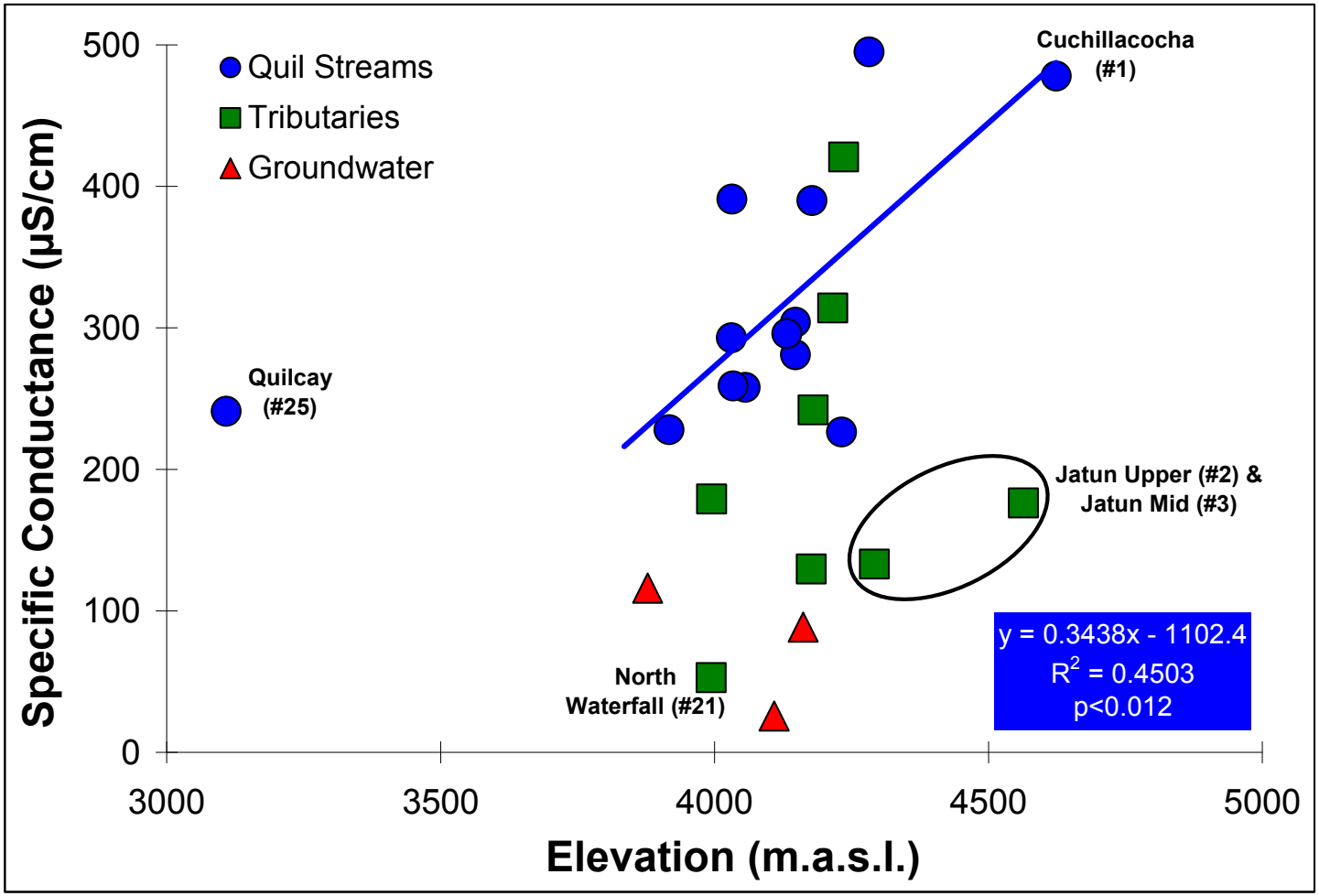

Figure 6 – Specific Conductance versus Local Time (24 hours) at Quil Bel Conf
Specific conductance at this site is theorized to correlate with glacier meltwater contribution. The maximum specific conductance value corresponds to peak glacial meltwater contribution (14:30) while the lowest specific conductance value corresponds to a minimum meltwater contribution (7:30).

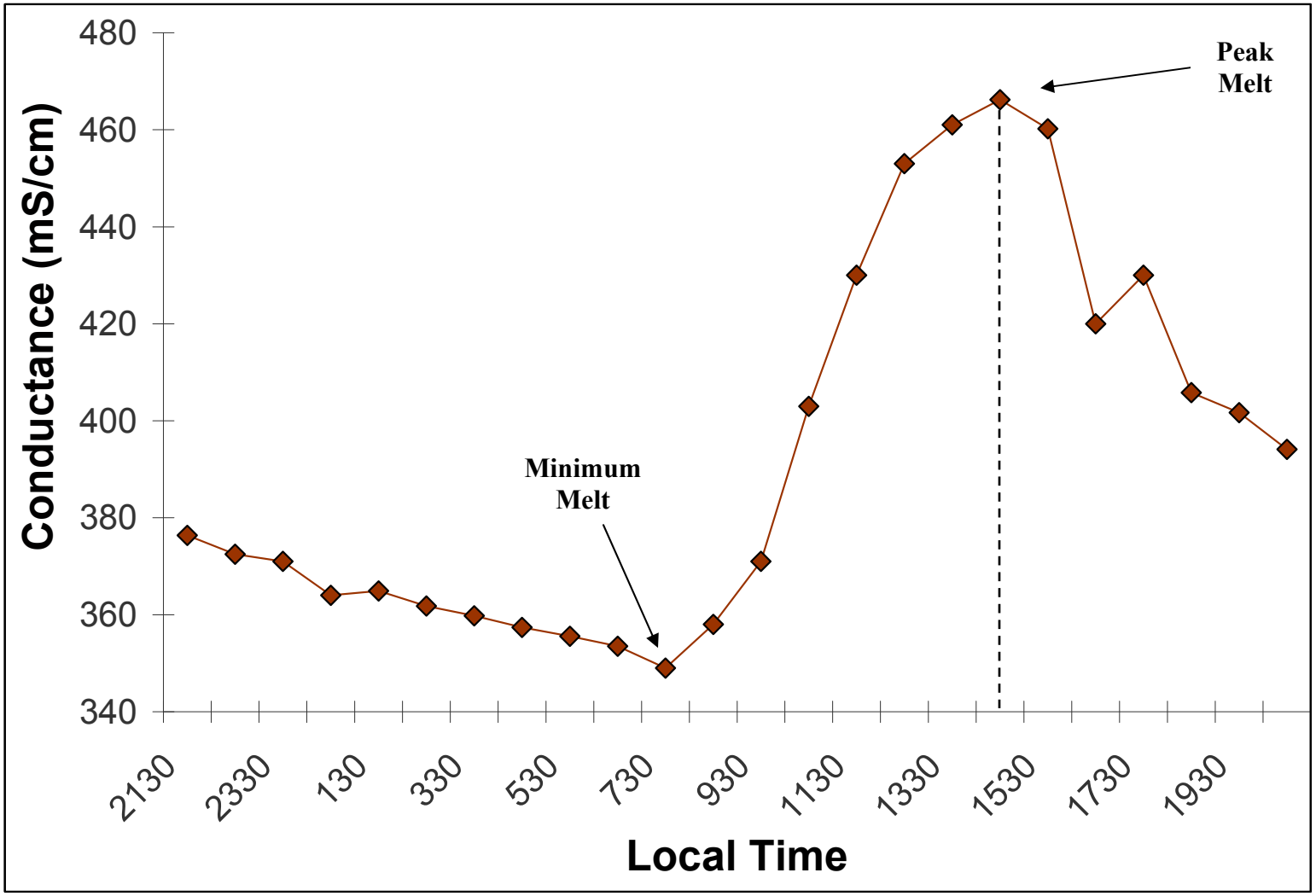

Figure 7 – Average Percentage of Ions Relative to TZ+ or TZ- by Site in Quilcayhuanca
Cations and anions of each of five groups are plotted relative to total average positive charge of their group (TZ+) and total average negative charge of their group, respectively. Surface water and groundwater differ in a number of ways. The ionic composition of groundwater is relatively similar to the ionic composition of the Rio Santa.

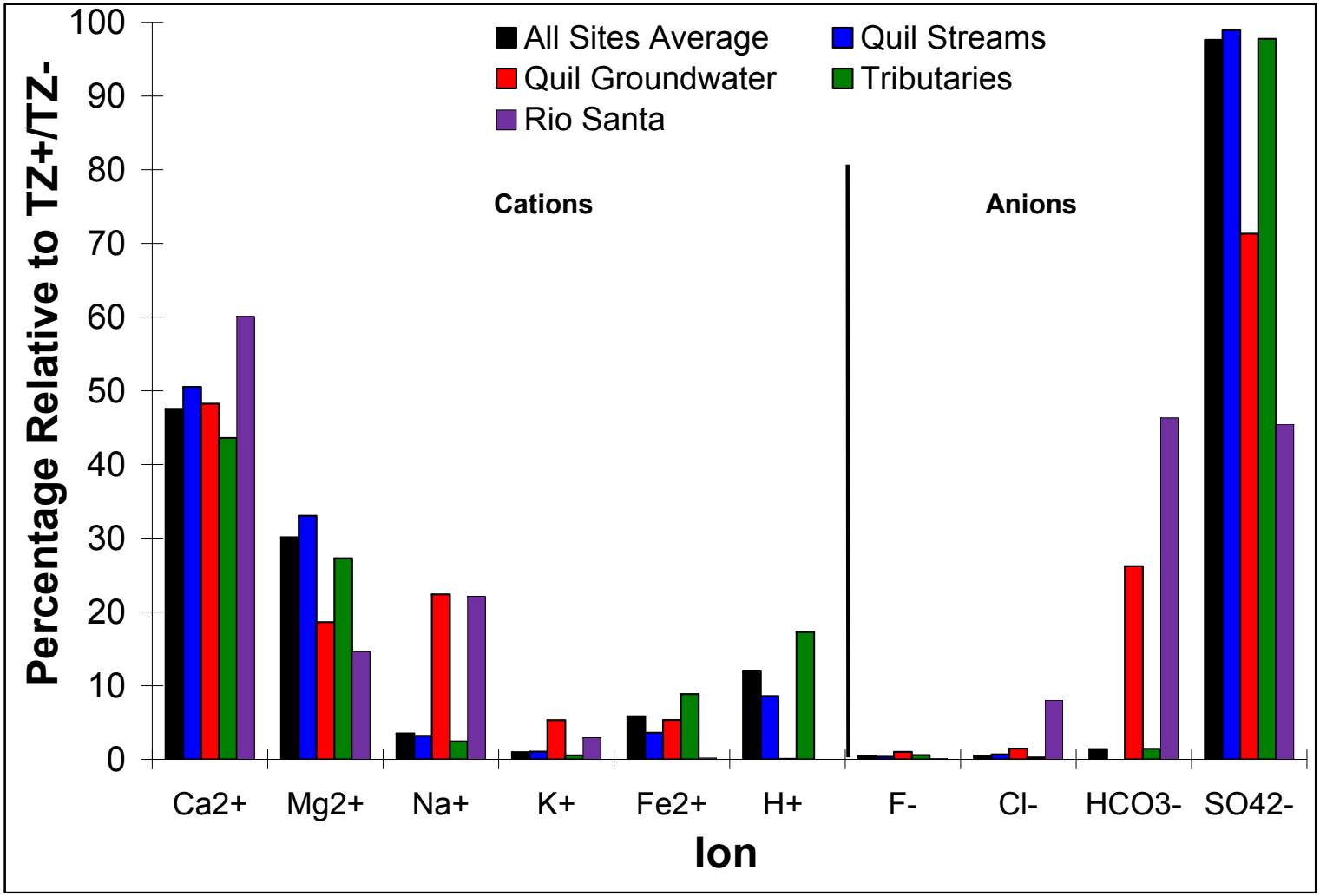

Figure 8 – Piper Diagram with Average Compositions of Groups from Quilcayhuanca, the Rio Santa, and Cord. Negra
This Piper diagram displays the average ionic composition of groups in Quilcayhuanca and also the overall average ionic composition from Quilcayhuanca. The diagram also displays the average ionic compositions for the Rio Santa and Cordillera Negra. Groundwater samples from Quilcayhuanca fall on a mixing line with the Rio Santa and Cordillera Negra. Note that ionic compositions have not been corrected for discharge.

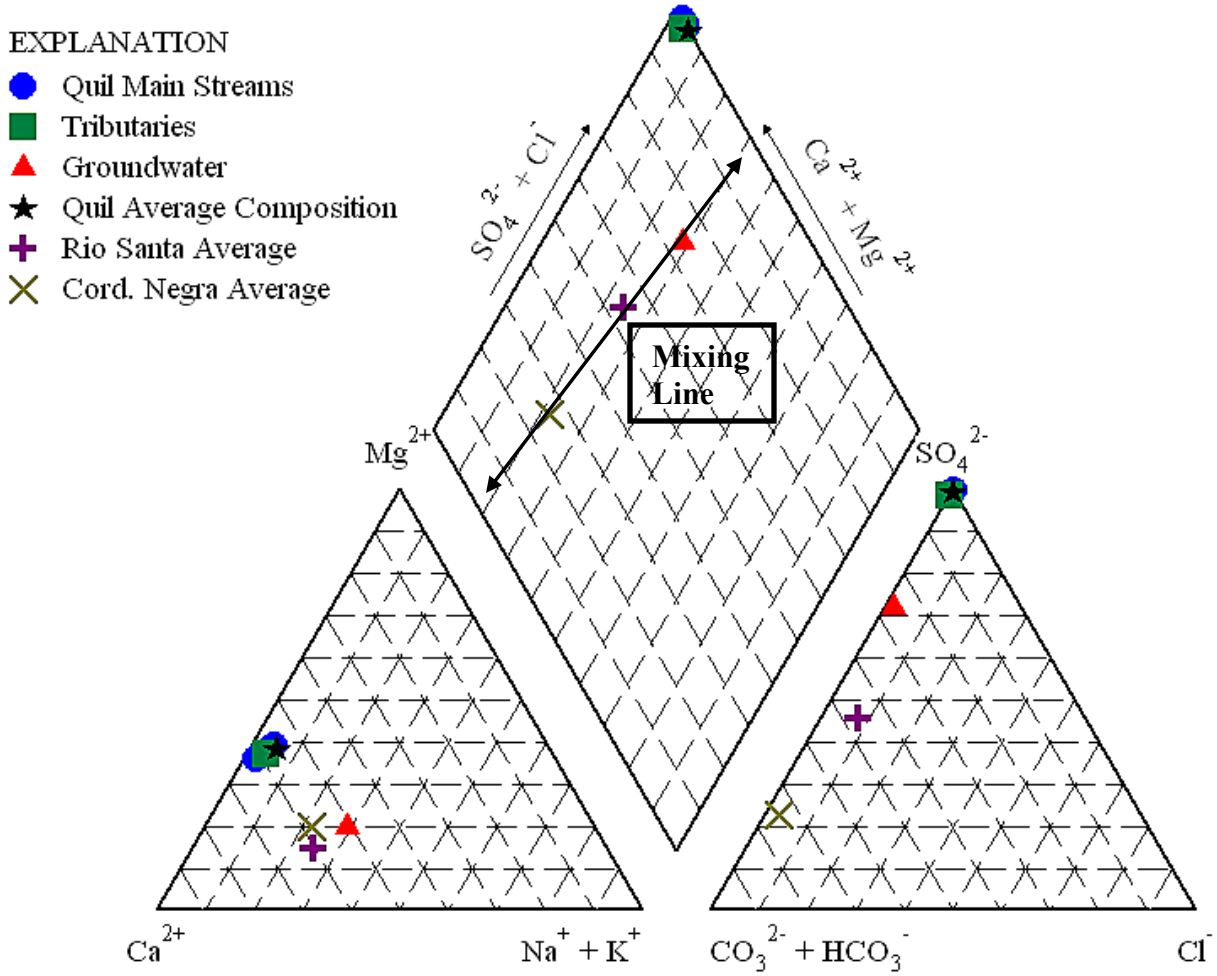

Figure 9 – Total P versus Elevation for Sampling Sites in Quilcayhuanca
Groundwater (with the exception of #23) and sites #2, #3, and #21 have the lowest total P concentrations likely because they have the highest pH. No trend is observed between total P and elevation for the group Quil Streams. The blue, dotted line indicates that the trend line for Quil Streams is not significant at the 5% level of significance.

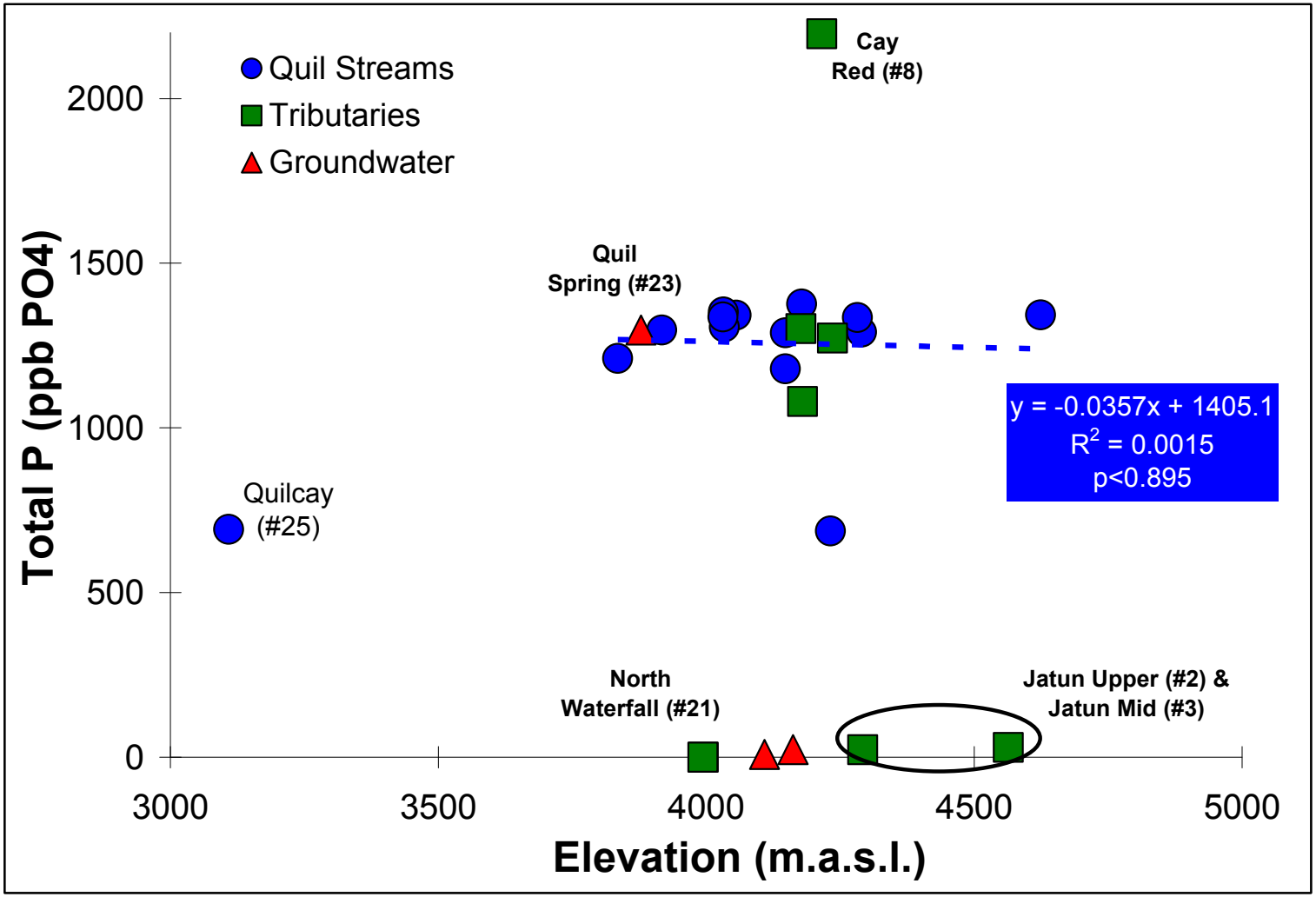

Figure 10 – Total N versus Elevation for Sampling Sites in Quilcayhuanca
No trend was observed between total N and elevation. There is no distinction between groundwater and surface water sites. The blue, dotted line indicates that the trend line for Quil Streams is not significant at the 5% level of significance.

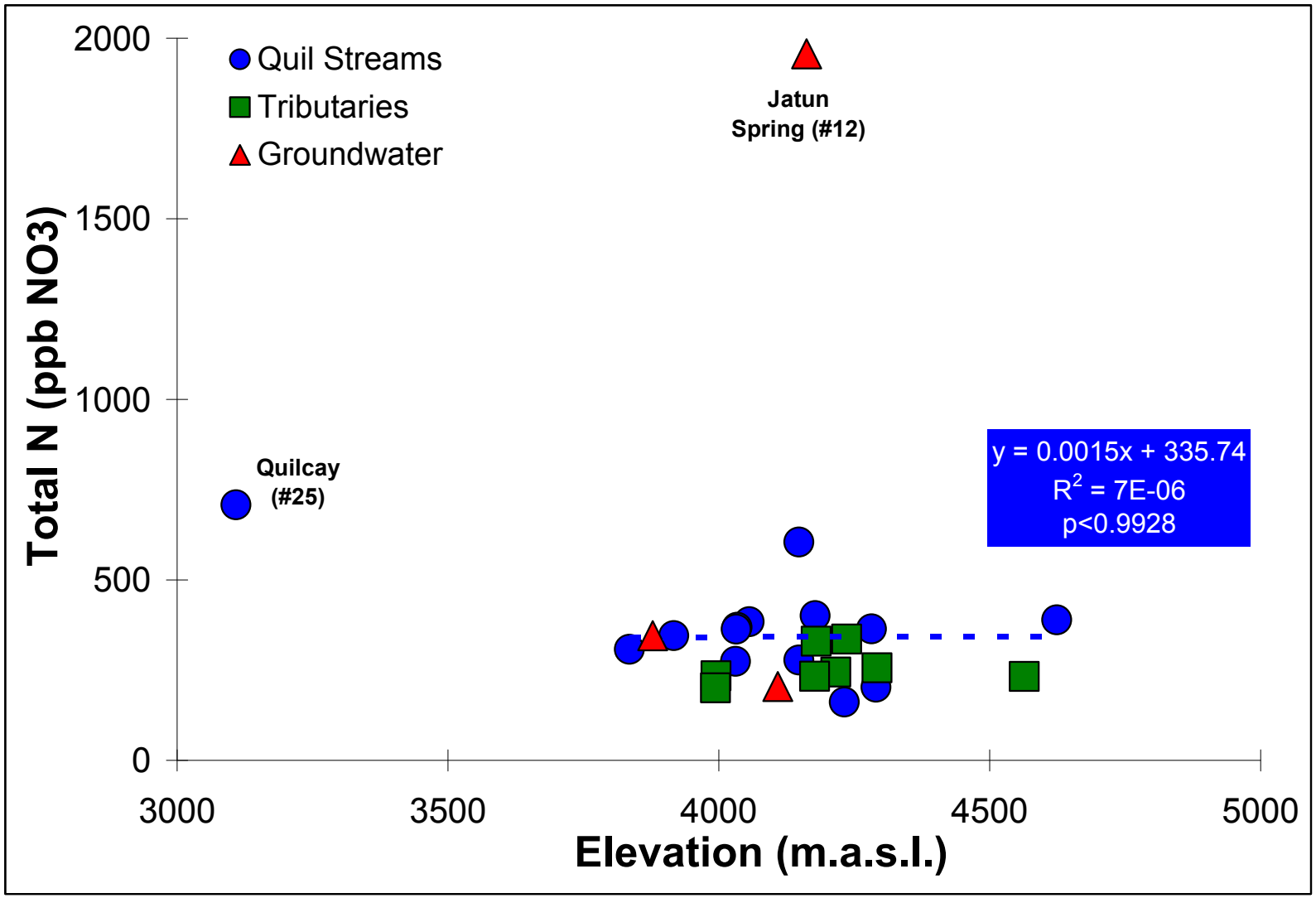

Figure 11 – Si versus Elevation for Sampling Sites in Quilcayhuanca
Two of the three groundwater samples have the highest Si concentrations. Si increases with decreasing elevation for Quil Streams. The site Quilcay (#25) is excluded from this trend line because it is outside of the drainage basin. The blue, dashed line indicates that this trend line is not quite statistically significant at the 5% significance level.

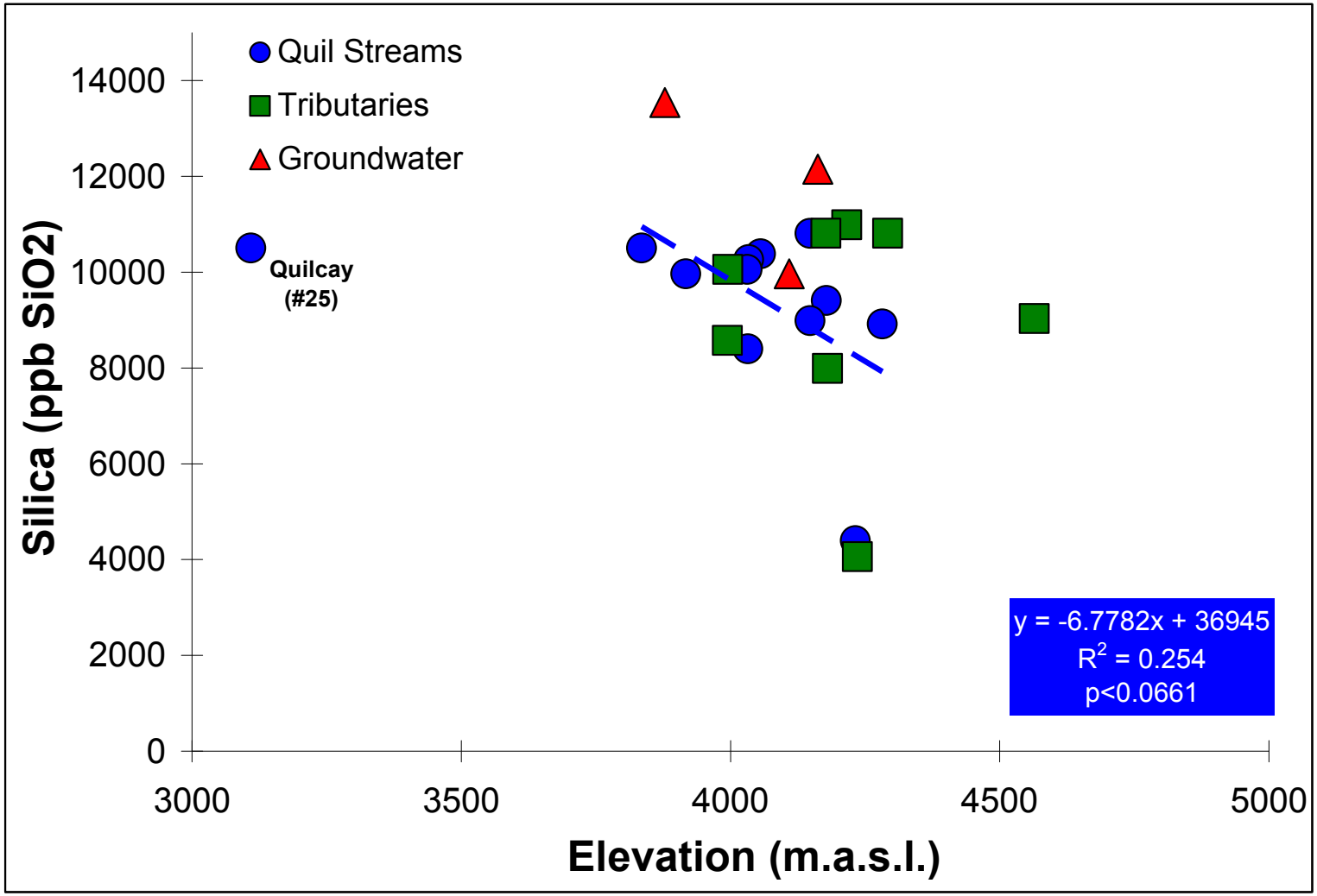

Figure 12 – $\delta^{18}O$ versus Elevation for Sampling Sites in Quilcayhuanca
In general, groundwater sites have more positive $\delta^{18}O$. For the group Quil Streams, excluding Quilcay (#25) because it is outside of the drainage basin, $\delta^{18}O$ decreases with increasing elevation at a rate of -0.155‰ per 100 m rise. The solid blue line indicates that this trend is significant at the 5% significance level.

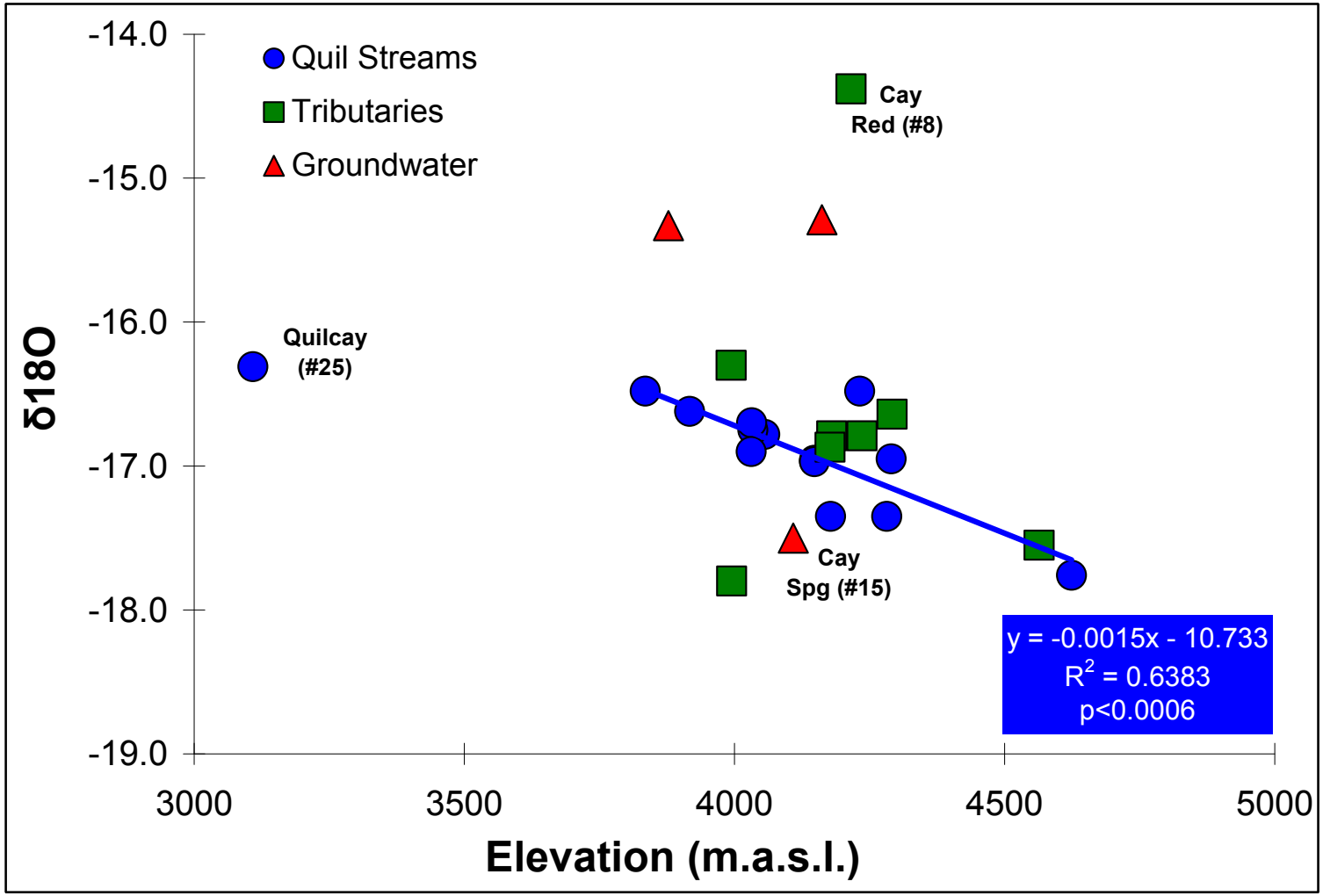

Figure 13 – $\delta^{18}O$ versus $\delta^{2}H$ for Sampling Sites in Quilcayhuanca
Samples from Quilcayhuanca fall off of the global Meteoric Water Line (MWL). This is attributed to evaporation which is fitting with dry season sampling. The dark blue line is fit through all Quilcayhuanca samples and represents the local meteoric water line.

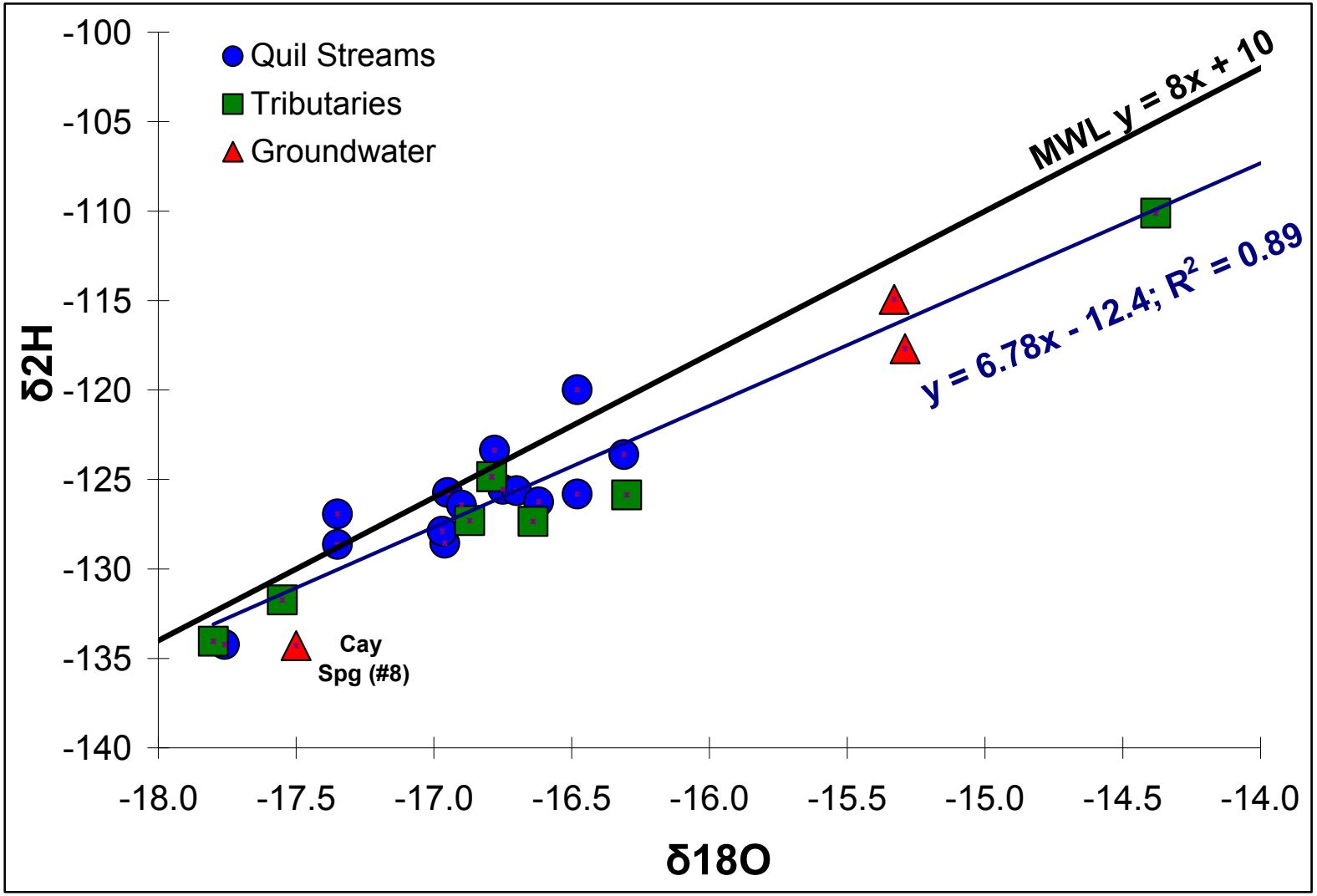

Figure 14 – Average $\delta^{18}O$ versus Average $\delta^{2}H$ for Quilcayhuanca, Rio Santa, and Cord. Negra
Average $\delta^{18}O$ and $\delta^{2}H$ for Quilcayhuanca, the Rio Santa, and the Cordillera Negra are plotted with 1 standard deviation to represent mixing. As expected, the Rio Santa is a mixture of the more negative isotopic values from Quilcayhuanca and the more positive values from the nonglacierized Cordillera Negra.